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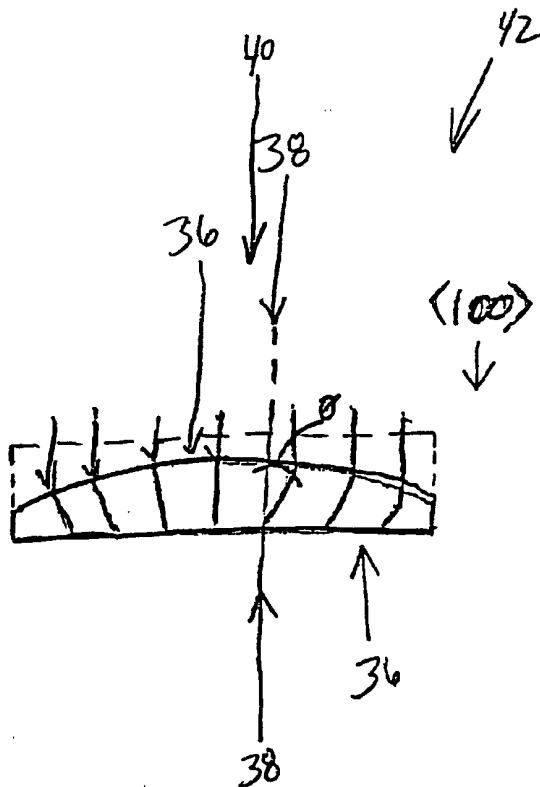
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[Continued on next page]

(54) Title: PREFERRED CRYSTAL ORIENTATION OPTICAL ELEMENTS FROM CUBIC MATERIALS

(57) Abstract: The invention provides a method of making a <194 nm wavelength calcium fluoride crystal optical lithography element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence by providing an optical element optical calcium fluoride crystal with an input face {100} crystal plane and forming the input face {100} crystal plane into an optical lithography element surface of an optical lithography element having an optical axis, with the optical axis aligned with a <100> crystal direction of the optical calcium fluoride crystal. In a preferred embodiment, the below 194 nm transmitting optical element is a <100> oriented calcium fluoride lens. In a preferred embodiment, the below 194 nm transmitting optical element is a <100> oriented calcium fluoride beam splitter.



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PREFERRED CRYSTAL ORIENTATION OPTICAL ELEMENTS FROM CUBIC MATERIALS

[0001] This application claims the benefit of, and incorporates by reference, U. S. Provisional Application, 60/291,424 filed May 16, 2001 by N.F. Borrelli, D.C. Allan, C.M. Smith, and B.D. Stone entitled PREFERRED CRYSTAL ORIENTATION OPTICAL ELEMENTS FROM CUBIC MATERIALS.

FIELD OF THE INVENTION

[0002] The present invention relates generally to short wavelength optical systems and elements for use therein, optical projection lithography methods and photolithography, and particularly to optical photolithography fluoride crystal elements for use in optical photolithography systems and short wavelength optical systems utilizing ultraviolet light (UV) wavelengths below 194 nm, such as UV lithography systems utilizing wavelengths in the 193 nm region and the 157 nm region.

TECHNICAL BACKGROUND

[0003] Projection optical photolithography methods/systems that utilize the ultraviolet wavelengths of light below 194 nm provide benefits in terms of achieving smaller feature dimensions. Such methods/systems that utilize ultraviolet wavelengths in the 157 nm and the 193 nm wavelength regions have the potential of improving the manufacturing of integrated circuits with smaller feature sizes but the commercial use and adoption of below 194 nm UV in high volume mass production of integrated circuits has been slow. Part of the slow progression to below 194 nm UV by the semiconductor industry has been due to the lack of economically manufacturable fluoride cubic crystal optical elements with high performance at such short wavelengths. For the benefit of ultraviolet photolithography in the 157 nm region such as the emission spectrum window of a fluorine excimer laser and the 193 nm region such as the ArF excimer laser emission spectrum to be utilized in the manufacturing of integrated circuits there is a need for fluoride crystal optical

elements that have beneficial optical properties and that can be designed for and utilized with below 194nm UV photons. The Argon Fluoride emits at ~193 nm and the Fluorine (F₂) excimer emits at ~157 nm, and for various optical applications it is preferable to have such short wavelengths of light less than 194 nm. For use with optical systems with Fluorine (F₂) lasers or Argon Fluoride lasers, the preferred crystal material for optical elements has been calcium fluoride, a cubic fluoride crystal.

SUMMARY

[0004] The invention includes a method of making a < 194 nm wavelength transmitting calcium fluoride crystal optical lithography element for transmitting wavelengths less than about 194 nm along an optical axis with minimal intrinsic birefringence. The method includes providing an optical element calcium fluoride crystal with an input face {100} crystal plane and forming said input face {100} crystal plane into an optical lithography element surface of an optical lithography element having an optical axis, with the optical axis aligned with a <100> crystal direction of the calcium fluoride crystal.

[0005] The invention includes a <194 nm wavelength transmitting calcium fluoride crystal optical lithography element for transmitting wavelengths less than 194 nm with minimal intrinsic birefringence. The optical lithography element is comprised of an optical calcium fluoride crystal with a {100} crystal plane and a <100> crystal direction with the optical element having an optical axis aligned with the <100> calcium fluoride crystal direction.

[0006] The invention includes a method of making a fluoride crystal optical element for transmitting short wavelengths of light (<194 nm) along an optical axis with minimal intrinsic birefringence. The method includes providing an optical element optical fluoride crystal with an input face {100} crystal plane and forming the input face {100} crystal plane into an optical element surface of an optical element having an optical axis with the optical axis aligned with a <100> crystal direction of the optical fluoride crystal.

[0007] The invention includes an optical element for transmitting wavelengths less than about 194 nm with minimal intrinsic birefringence. The optical element is comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction with the optical element having an optical axis aligned with the <100> crystal direction.

[0008] The invention includes a below 194 nm wavelength transmitting lens with minimal intrinsic birefringence comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction. The lens has a curved optical surface and an optical axis aligned with the <100> crystal direction and normal to the {100} crystal plane.

[0009] The invention includes a below 194 nm wavelength transmitting beam splitter cube with minimal intrinsic birefringence. The beam splitter cube is comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction with the beam splitter cube face parallel to the {100} crystal plane and an optical axis aligned with the <100> crystal direction.

[0010] Additional features and advantages of the invention will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the invention as described in the written description and claims hereof, as well as the appended drawings.

[0011] It is to be understood that both the foregoing general description and the following detailed description are merely exemplary of the invention, and are intended to provide an overview or framework to understanding the nature and character of the invention as it is claimed.

[0012] The accompanying drawings are included to provide a further understanding of the invention, and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiment(s) of the invention, and together with the description serve to explain the principles and operation of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1, 1(a) and 1(b) show an embodiment of the invention with a $\langle 100 \rangle$ crystal direction oriented fluoride crystal lens element.

[0014] FIG. 2 and 2(a) show an embodiment of the invention with a $\langle 100 \rangle$ crystal direction oriented fluoride crystal beam splitter element.

[0015] FIG. 3 and 3(a) show an embodiment of the invention with a $\langle 100 \rangle$ crystal direction oriented fluoride crystal beam splitter element.

DETAILED DESCRIPTION

[0016] The invention includes a method of making a $\langle 194 \text{ nm} \rangle$ wavelength transmitting calcium fluoride crystal optical lithography element 30 for transmitting wavelengths less than about 194 nm, such as 193 nm or 157 nm, along an optical axis with minimal birefringence. The method includes providing an optical element optical calcium fluoride crystal 32 with an input face $\{100\}$ crystal plane 34. The method includes forming the input face $\{100\}$ crystal plane 34 into an optical lithography element surface 36 of the optical lithography element 30 having an optical axis 38 with the optical axis 38 aligned with a $\langle 100 \rangle$ crystal direction 40 of the optical calcium fluoride crystal 32. In an embodiment, forming includes forming the calcium fluoride crystal 32 into a lens element 42 with a curved optical element surface 44. The formed lens element 42 having a lens optical axis 38 aligned with a $\langle 100 \rangle$ crystal direction 40 of the calcium fluoride crystal and normal to the $\{100\}$ calcium fluoride crystal plane 34. In an embodiment, forming includes forming the optical calcium fluoride crystal 32 into a beam splitter cube 46 with a beam splitter cube face 48 parallel to the $\{100\}$ calcium fluoride crystal plane 34 and a beam splitter optical axis 38 aligned with a $\langle 100 \rangle$ crystal direction 40 of crystal 32.

[0017] The invention includes a $\langle 194 \text{ nm} \rangle$ wavelength calcium fluoride crystal optical lithography element 30 for transmitting wavelengths less than 194 nm with minimal intrinsic birefringence. The optical lithography element 30 is comprised of an optical calcium fluoride crystal 32 with a $\{100\}$ crystal plane 34 and a $\langle 100 \rangle$ crystal direction 40. The optical element has an optical axis 38 aligned with the $\langle 100 \rangle$ calcium fluoride crystal direction 40. The optical element surface of the element is preferably normal to the optical axis 38, with the optical surface formed in

alignment with the crystals {100} crystal plane. In an embodiment the calcium fluoride crystal optical element is a lens. In an embodiment the calcium fluoride crystal optical element is a beam splitter.

[0018] The invention includes a method of making a fluoride crystal optical element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence. Preferably the method includes making a cubic fluoride crystal optical lithography element for lithography systems that operate at less than 194 nm, such as 193 wavelengths or 157 nm wavelengths. The method includes providing an optical element optical fluoride crystal 32 with an input face {100} crystal plane 34 and forming the face {100} plane into an optical element surface 36 of an optical element 30 having an optical axis 38 aligned with a <100> crystal direction 40 of the optical fluoride crystal 32. In an embodiment, forming includes forming the optical fluoride crystal 32 into a lens element 42 with a curved optical element surface 44, with the lens element 42 having a lens optical axis 38 aligned with a <100> crystal direction 40 of crystal 32 and normal to the {100} crystal plane 34 of crystal 32. In a preferred embodiment crystal 32 is formed into a lens element 42 for directing a cone of light rays having a cone angle θ of at least 35.26°. In another embodiment, crystal 32 is formed into a beam splitter cube 46 with a beam splitter cube face 48 parallel to the {100} crystal plane 34 and a beam splitter optical axis 38 aligned with a <100> crystal direction 40 of crystal 32. In a preferred embodiment the crystal 32 is formed into a beam splitter cube for use with a curved mirror to deliver a polarized light having a <194 nm wavelength, with incoming light rays incident at an angle onto the cube. In a preferred embodiment the crystal 32 is formed into an interferometry beam splitter cube for use below 194 nm light rays, with light rays travelling along the optical axis in alignment with the <100> directions ([100], [010], [001]) of crystal 32. In a preferred embodiment crystal 32 is formed into an optical element 30 with minimized intrinsic birefringence with element for use in below 194 nm optical applications when light through the optical element is not perpendicular to the {100} crystal planes. In an embodiment optical fluoride crystal 32 is comprised of calcium, preferably comprised of calcium fluoride and most preferably consists essentially of CaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment optical fluoride crystal 32 is comprised of

barium, preferably comprised of barium fluoride, and most preferably consists essentially of BaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment optical fluoride crystal 32 is comprised of strontium, preferably comprised of strontium fluoride, and most preferably consists essentially of SrF_2 with a below 194 nm internal transmission of at least 99%/cm.

[0019] The invention includes an optical element for transmitting wavelengths less than about 194 nm with minimal intrinsic birefringence. The optical element is comprised of a cubic optical fluoride crystal with a {100} crystal plane and a $\langle 100 \rangle$ crystal direction with the optical element having an optical axis aligned with the $\langle 100 \rangle$ crystal direction. In a preferred embodiment, the element is a below 194 nm lithography element for transmitting a below 194 nm lithography wavelength such as a 193 nm wavelength or a 157 nm wavelength in an optical lithography system. The optical element 30 transmits below 194 nm light along an optical axis 38. The optical element 30 is comprised of a cubic optical fluoride crystal 32 with a {100} crystal plane 34 and a $\langle 100 \rangle$ crystal direction 40, with the optical axis 38 aligned with a $\langle 100 \rangle$ crystal direction 40 and normal to a {100} crystal plane 34. The optical element 30 has an optical element surface 36 that is aligned with a {100} crystal plane and normal to a $\langle 100 \rangle$ crystal direction optical axis of the element. In an embodiment the optical fluoride crystal 32 of element 30 is comprised of calcium, preferably calcium fluoride, and most preferably the crystal consists essentially of CaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the optical fluoride crystal 32 of element 30 is comprised of barium, preferably barium fluoride, and most preferably the crystal consists essentially of BaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the optical fluoride crystal 32 of element 30 is comprised of strontium, preferably strontium fluoride and most preferably the crystal consists essentially of SrF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment optical element 30 is a lens element with a curved optical surface and a lens optical axis 38 aligned with the $\langle 100 \rangle$ crystal direction. Preferably the lens element has a cone angle θ for a cone of light rays with the cone angle at least 35.26° , with the light rays not perpendicular to the {100} crystal planes. In an embodiment optical element 30 is a beam splitter cube with a beam splitter cube

face 48 parallel to the {100} crystal plane and a beam splitter optical axis aligned with the <100> crystal direction. In a preferred embodiment the beam splitter cube is a lithography element for use with the curved mirror to deliver a polarized light having a <194 nm wavelength, preferably with incoming light rays incident at an angle onto the cube. In a preferred embodiment, the beam splitter cube is an interferometry beam splitter cube for use with below 194 nm light rays with light rays travelling along the optical axis in alignment with the <100> crystal directions. The optical element 30 provides for minimized intrinsic birefringence at short wavelengths below 194 nm.

[0020] The invention includes a below 194 nm wavelength transmitting lens 42 comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction with the lens having a curved optical surface 44 and an optical axis 38. The lens optical axis 38 is aligned with the <100> crystal direction and normal to the {100} crystal plane. In a preferred embodiment the below 194 nm transmitting lens optical fluoride crystal is comprised of calcium, preferably calcium fluoride and most preferably consists essentially of CaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the below 194 nm transmitting lens optical fluoride crystal is comprised of barium, preferably barium fluoride, most preferably the crystal consists essentially of BaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the below 194 nm transmitting lens optical fluoride crystal is comprised of strontium, preferably strontium fluoride crystal, and most preferably the crystal consists essentially of SrF_2 with a below 194 nm internal transmission of at least 99%/cm. Preferably the lens element has a cone angle θ for a cone of light rays with the cone angle at least 35.26° . Preferably the optical element crystal lens provides for minimized intrinsic birefringence at short wavelength light rays below 194 nm that are non perpendicular to the {100} crystal plane 34.

[0021] The invention includes a below 194 nm wavelength transmitting beam splitter cube 46 comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction with the beam splitter cube having a beam splitter cube face 48 parallel to the {100} crystal plane and having a beam splitter optical axis aligned with the <100> crystal direction. In a preferred embodiment the below 194

nm beam splitter cube optical fluoride cubic crystal is comprised of calcium, preferably calcium fluoride, and most preferably the cubic crystal consists essentially of CaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the below 194 nm beam splitter cube optical fluoride cubic crystal is comprised of barium, preferably barium fluoride and most preferably consists essentially of BaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the below 194 nm beam splitter cube optical fluoride cubic crystal is comprised of strontium, preferably strontium fluoride and most preferably consists essentially of SrF_2 with a below 194 nm internal transmission of at least 99%/cm. In a preferred embodiment the beam splitter cube 46 is a lithography element for use with lithography wavelengths such as 193 or 157 nm. Preferably the lithography element beam splitter is for use with a curved mirror to deliver a polarized light having a <194 nm wavelength preferably with incoming light rays incident at an angle onto a cube face 48. In a preferred embodiment the beam splitter cube 46 is a interferometry optical element for use with below 194 nm light rays with light rays travelling along the axis aligned with a <100> direction of the crystal. The beam splitter cube optical element 46 provides for minimizing intrinsic birefringence at short wavelengths below 194 nm by utilizing the <100> crystal directions of the cubic fluoride crystal 32.

[0022] Up until now the concern with cubic crystals with respect to birefringence has been related to that associated with stress birefringence, as a consequence of the growth process. This has pointed to a preferred direction for use the crystals with the incident plane being {111}, the plane where the effect of the stress birefringence is minimized.

[0023] However there is an intrinsic birefringence in cubic crystals that has not been considered. This birefringence has nothing to do with stress. The intrinsic birefringence becomes comparable to the stress birefringence at shorter wavelengths. Intuition suggests that cubic crystalline materials, such as CaF_2 or BaF_2 , are optically isotropic. In other words, the index of refraction or dielectric tensor is the same for light propagation in any arbitrary direction. In this way, cubic crystals resemble glasses, with isotropic optical properties. For cubic crystals it turns out that this picture is only valid in the limit in which the light wavelength is very long

compared with interatomic dimensions. As the material is used at shorter wavelengths additional contributions to the optical response are no longer negligible. These additional contributions create a directionally dependent index of refraction, i.e. intrinsic birefringence. It is important to note that this birefringence is not stress-related birefringence. It is an intrinsic property of any cubic crystal and is not removable by annealing.

[0024] It is shown that this intrinsic birefringence vanishes for light propagating in the symmetry directions $\langle 111 \rangle$ or $\langle 100 \rangle$, but reaches its maximum value for light going in the $\langle 110 \rangle$ directions.

[0025] It has been the practice to fabricate optics of CaF_2 by using the $\{111\}$ crystal plane to form the input face of the optic. The fabrication of an optic where light will be propagating through it in directions other than normal to the $\{111\}$ plane (or equivalently high symmetry directions) presents a case where the intrinsic birefringence described here could be an issue.

[0026] Three examples are shown in the attached FIGs. The first two examples are related to imaging applications at short wavelengths. The first case is where the optic itself has curvature (FIG. 1). Consider an example case that includes a cone of light rays at an angle θ of at least $\cos^{-1}(2/6^{1/2}) = 35.26$ degrees. In that cone $\langle 110 \rangle$ directions are included and peak birefringence should be observed at several locations. Of the 12 equivalent $\langle 110 \rangle$ directions only 3 lie within less than 90 degrees of $[111]$. These are $[110]$, $[101]$ and $[011]$. Since the cone of light includes these three directions, three equivalent peaks in birefringence should be observed 120 degrees apart in the transmitted intensity. If one considers a similar case except now using the $\{100\}$ plane as the incident face, it can be shown that the cone of incidence sweeps a larger angle for the same birefringence. Alternatively expressed, the same cone angle has less birefringence when the $\{100\}$ plane is used.

[0027] The second example is where one would use a curved mirror in association with a flat cube beam splitter (FIG. 2) to deliver polarized light. A quarter wave plate is also included in this design. In this case, due to the reflection from the curved mirror, the incoming rays are incident at an angle onto the cube. This is a

related situation to that shown in Figure 1 and here again the {100} face should offer an advantage in minimizing inherent birefringence.

[0028] Finally, interferometry applications that utilize calcium fluoride would also benefit from the recognition of the utility of the {100} plane. A schematic of this is shown in FIG. 3. If ray 1 travels in the $\langle 111 \rangle$ direction, then it experiences no intrinsic birefringence. However, in this case, ray 3 must travel in one of the $\langle 110 \rangle$ directions because these are at right angles to the $\langle 111 \rangle$ direction, experiencing maximum intrinsic birefringence.

[0029] Alternatively, if ray 1 travels in the $\langle 100 \rangle$ direction of the crystal, then ray 3 can travel in the $\langle 010 \rangle$ direction. Both of these directions have zero intrinsic birefringence. This approach would negate the use of a waveplate in the interferometer design.

[0030] The relevance of using the orientation that minimizes the amount of intrinsic birefringence encountered is in applications where wavefront integrity is critical. That would include short wavelength lithography and interferometry functions.

[0031] Intrinsic birefringence is zero in the {111} and {100} planes of cubic crystals and maximized in the {110} plane. It is proposed that the {100} plane is preferable for minimizing the effects of inherent birefringence, particularly when light through the optic is not perpendicular to the crystal plane.

[0032] In FIG. 3, with the cube beam splitter, light enters along path 1 and is split into paths 2 and 3 with equal path length through material. Intrinsic birefringence is zero in the $\langle 111 \rangle$ directions and zero in $\langle 111 \rangle$ and $\langle 100 \rangle$ directions. To avoid the effects of the naturally occurring birefringence, we fabricate a cubic optic such that the {100} face (or equivalent) of the crystal is the input face of the optic. In this case, ray 3 shown in FIG. 3 will emerge from the {010} face or equivalent of {100}. Thus the incident, transmitted, and reflected rays of FIG. 3 will experience no intrinsic birefringence.

[0033] This describes a simple physical picture of intrinsic birefringence of CaF_2 and other cubic crystals and also mathematical analysis of an intrinsic birefringence in cubic crystals that is only observable at short wavelength.

[0034] Ordinarily, cubic crystals such as CaF_2 are considered to have negligible intrinsic birefringence because of their cubic symmetry. (We are not considering birefringence induced by residual stresses.) However, as the light wavelength decreases, light waves experience a slightly different environment for different directions of propagation. Quantitatively, this effect is manifested as an additional symmetry-breaking term giving rise to intrinsic birefringence that is proportional to the inverse square of wavelength. This level of birefringence can be detrimental to optical performance at 157 nm and 193 nm.

[0035] The symmetry-breaking term proportional to $1/\lambda^2$, discussed is expected to occur in cubic systems from fundamental principles. Likewise, this term is absent from completely isotropic materials like glasses. The intrinsic birefringence vanishes for certain high symmetry directions of propagation, like $\langle 111 \rangle$ and $\langle 100 \rangle$, and reaches its maximum value for the in-between directions $\langle 110 \rangle$. Thus, for example, light traveling down a typical optic axis in the $\langle 111 \rangle$ direction will experience no intrinsic birefringence.

[0036] There is a rough estimate of the size of the intrinsic value, due to H. A. Lorentz, Collected Papers III, page 314:

$$\Delta n = 0.44\pi n(n^2 - 1)^2 (a / \lambda)^2 \quad (0.1)$$

where Δn is the birefringence, n is the index of refraction, "a" is a characteristic length that may be taken as a typical bond length, and λ is the wavelength of light. To get an estimate for $\lambda = 147\text{nm}$, take a literature value of $n=1.589$ and a bond length of 0.2365 nm for CaF_2 to get $\lambda n = 13 \times 10^{-6}$ or 130 nm/cm. The Lorentz estimate is believed to be on the high side by about a factor of 5. Consider this a very rough approximation with the correct $1/\lambda^2$ dependence.

[0037] To appreciate why the effect is largest in $\langle 110 \rangle$ directions and vanishes in $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, it suffices to consider the symmetries of a cube. If you look down an x, y, or z axis of a cube (i.e. $\langle 100 \rangle$ direction), you find that a 4-fold rotation carries the cube back into coincidence. Similarly, if you look down a body diagonal (i.e. $\langle 111 \rangle$ direction), you find a 3-fold symmetry rotation. Either of these symmetry rotations is enough to mix the components of any two-dimensional vector lying in the plane perpendicular to the rotation axis, destroying any birefringence for light waves traveling straight down either axis. If you look down the

cube in a $\langle 110 \rangle$ direction (e.g. looking down a line that runs across a cube face), you see an obviously rectangular symmetry that has only a 2-fold rotational symmetry. A 2-fold rotation does not mix vector components, so birefringence is possible. This turns out to be the direction of highest birefringence.

[0038] Before jumping into the mathematics, consider one more picture for light cone birefringence. With a cone of light whose average direction is $\langle 111 \rangle$; if the cone includes rays at an angle of at least $\cos^{-1}(\frac{2}{\sqrt{6}}) = 35.26^\circ$ (designs can reach 42° in the CaF_2), then $\langle 110 \rangle$ directions are included and peak birefringence should be observed at several locations. Of the 12 equivalent $\langle 110 \rangle$ directions, only three lie within less than 90° of $\langle 111 \rangle$. These are $[110]$, $[101]$, and $[011]$. Since the cone of light includes these three directions, three equivalent peaks in birefringence should be observed 120° apart in the transmitted intensity.

[0039] This section of mathematical details starts with the fundamental expression for the dielectric tensor, that is derivable from first principles, and derives several important expressions and results. This section is important to prove the vanishing of the intrinsic birefringence along $\langle 100 \rangle$ and $\langle 111 \rangle$, to show the vanishing of the intrinsic birefringence in isotropic materials (a kind of check on the algebra), and to show the nonzero result for the $\langle 110 \rangle$ directions. For light in the $\langle 110 \rangle$ direction, the detailed analysis also provides the directions of the principal optic axes.

[0040] The general expression for the dielectric tensor, including nonzero photon wavevector \vec{q} , is

$$\epsilon_{\mu\nu}(\vec{q}) = \epsilon_{\mu\nu}(\vec{q} = 0) + R_{\mu\nu ij} q_i q_j \quad (0.2)$$

where $R_{\mu\nu ij}$ is a new rank 4 tensor that accounts for the influence of nonzero wavevector on ϵ . This expression is derivable from fundamental quantum mechanics for optical response. Most conventional derivations take the $\vec{q} \rightarrow 0$ limit because that is usually a very good approximation. To preserve a close analogy to the rank 4 elasto-optical or photoelastic tensor p_{ijkl} relating strain and index change, we define the q -dependent index change as

$$\Delta B_{\mu\nu} = P_{\mu\nu ij} q_i q_j \quad (0.3)$$

where $\Delta B_{\mu\nu}$ is the change of the relative dielectric impermeability tensor B_{ij} from its $q=0$ value. (B_{ij} and related tensors are defined and discussed on page 243 of J. F. Nye, *Physical Properties of Crystals*. B_{ij} is the inverse of the dielectric tensor.) The tensor $P_{\mu\nu ij}$ we define here may or may not be defined the same way so a careful comparison is needed when working with actual values. In a cubic crystal system, a rank 4 tensor has only three unique nonzero components. Using a contracted notation (see J. F. Nye, *Physical Properties of Crystals*, near page 248), these components are

$$\begin{aligned} P_{1111} &\rightarrow P_{11} \\ P_{1122} &\rightarrow P_{12} \\ P_{1212} &\rightarrow P_{44} \end{aligned} \quad (0.4)$$

or P_{11} , P_{12} , and P_{44} . Note that the same three tensor components fully characterize the photoelastic response of a cubic material (a different tensor, of course, but with the same transformation properties). The dyad formed by $\bar{q}\bar{q}$ has to be modified to conform to the contracted index notation. The 3x3 tensor (dyad) representing $\bar{q}\bar{q}$ is replaced by a column vector with 6 components

$$\bar{Q} = \begin{bmatrix} q_1 q_1 \\ q_2 q_2 \\ q_3 q_3 \\ 2q_2 q_3 \\ 2q_1 q_3 \\ 2q_1 q_2 \end{bmatrix}. \quad (0.5)$$

[0041] The factors of 2 are needed to make the contracted index products reproduce the messier index summations of the original rank 4 tensor. Using these definitions, Eq.(0.3) can be rewritten

$$\begin{aligned}
B_{11}(\vec{q}) &= B_{11}(0) + P_{11}q_1^2 + P_{12}(q_2^2 + q_3^2) \\
B_{22}(\vec{q}) &= B_{22}(0) + P_{11}q_2^2 + P_{12}(q_1^2 + q_3^2) \\
B_{33}(\vec{q}) &= B_{33}(0) + P_{11}q_3^2 + P_{12}(q_1^2 + q_2^2) \\
B_{32}(\vec{q}) &= 2P_{44}q_2q_3 \\
B_{31}(\vec{q}) &= 2P_{44}q_1q_3 \\
B_{21}(\vec{q}) &= 2P_{44}q_1q_2
\end{aligned} \tag{0.6}$$

[0042] Given measured or theoretically calculated values for the three constants P_{11} , P_{12} , and P_{44} , Eq.(0.6) shows exactly how the dielectric impermeability tensor components are modified at short wavelength in a cubic system. Further analysis requires that we specify some given direction for the photon wavevector \vec{q} so that we know the components q_1 , q_2 , and q_3 . (Note that different definitions of the P tensor are possible. The definitions should be checked carefully before comparing results.) The dielectric impermeability tensor is used to define the index ellipsoid or optical indicatrix by the expression

$$B_{ij}x_i x_j = 1. \tag{0.7}$$

[0043] Thus, small changes in B_{ij} give rise to changes in index of refraction (including birefringence) and changes in the principal index axes (the eigenvectors of B). For a cubic crystal (in the $\vec{q} = 0$ limit), the impermeability tensor is diagonal and has three identical eigenvalues, which are $(1/n^2)$ for index of refraction n . Thus $B_{11}(0)$, $B_{22}(0)$, and $B_{33}(0)$ for our cubic system are each $(1/n^2)$.

[0044] We expect birefringence along [100] to vanish according to arguments given above, but as a check, we apply Eq.(0.6) for $\vec{q} = (q, 0, 0)$. Then the dielectric impermeability tensor components become

$$\begin{aligned}
B_{11}(\vec{q}) &= 1/n^2 + P_{11}q^2 \\
B_{22}(\vec{q}) &= 1/n^2 + P_{12}q^2 \\
B_{33}(\vec{q}) &= 1/n^2 + P_{12}q^2 \\
B_{32}(\vec{q}) &= 0 \\
B_{31}(\vec{q}) &= 0 \\
B_{21}(\vec{q}) &= 0
\end{aligned} \tag{0.8}$$

[0045] Note that the dielectric impermeability tensor for this case is still diagonal, but no longer has the same value for each element on the diagonal. However, since light is a transverse wave, only the B_{22} and B_{33} components are relevant for our case of light traveling in the [100] direction. For this simple case there are two equal eigenvalues that correspond to any polarizations perpendicular to [100]. Intrinsic birefringence is the difference between these two equal values, i.e. zero. Even though the birefringence vanishes, the actual index of refraction is altered slightly by this term. The altered index of refraction is given by the expression

$$\Delta n = -\frac{1}{2}n^3\Delta B = -\frac{1}{2}n^3P_{12}q^2. \quad (0.9)$$

[0046] (See Nye again, page 252.) It will turn out that the index of refraction, whether birefringent or not, can be modified by terms of order 1 ppm for light propagation in different directions in the cubic crystal. Such intrinsic variation in the index of refraction should be accounted for in lens design modeling, in addition to the intrinsic birefringence.

The <111> case

[0047] As for <100>, we have given a symmetry argument for the vanishing of the birefringence for light propagation down the <111> axis. Nevertheless, it is instructive to go through the algebra and demonstrate this. Consider a wavevector $\vec{q} = (q, q, q)/\sqrt{3}$. The normalization is chosen so that the magnitude is q and not $\sqrt{3}q$. The dielectric impermeability tensor components become

$$\begin{aligned} B_{11}(\vec{q}) &= 1/n^2 + q^2(P_{11} + 2P_{12})/3 \\ B_{22}(\vec{q}) &= 1/n^2 + q^2(P_{11} + 2P_{12})/3 \\ B_{33}(\vec{q}) &= 1/n^2 + q^2(P_{11} + 2P_{12})/3 \\ B_{32}(\vec{q}) &= 2P_{44}q^2/3 \\ B_{31}(\vec{q}) &= 2P_{44}q^2/3 \\ B_{21}(\vec{q}) &= 2P_{44}q^2/3 \end{aligned} \quad (0.10)$$

[0048] Now the dielectric impermeability tensor is not diagonal, so it is not as obvious what the indices of refraction are for different polarizations and the related birefringence. What is needed are the eigenvectors and eigenvalues of the dielectric

impermeability tensor, giving the principal axes and principal indices of refraction (after some manipulation). The dielectric impermeability tensor has the form of a 3x3 matrix

$$\begin{bmatrix} a & b & b \\ b & a & b \\ b & b & a \end{bmatrix}. \quad (0.11)$$

[0049] This matrix has one eigenvalue of $(a+2b)$, with eigenvector $(1,1,1)/\sqrt{3}$, and two degenerate eigenvalues of $(a-b)$, with eigenvectors of $(-1,1,0)/\sqrt{2}$ and $(-1,0,1)/\sqrt{2}$. (Because the two eigenvalues are the same, any linear combination of these eigenvectors is also an eigenvector.) The first principal axis is along the propagation direction, so is irrelevant. The second two are possible principal axes of polarization, but again they do not produce birefringence because the eigenvalues (and indices of refraction) are the same. As in the $\{100\}$ case, the actual index of refraction is slightly modified, this time to the value

$$\Delta n = -\frac{1}{2}n^3\Delta B = -\frac{1}{2}n^3(P_{11} + 2P_{12} - 2P_{44})q^2/3, \quad (0.12)$$

[0050] but the intrinsic birefringence is zero.

The $\langle 110 \rangle$ case

[0051] We have argued from symmetry that the intrinsic birefringence will not vanish for the $\langle 110 \rangle$ direction.

[0052] The algebraic proof that follows also gives a quantitative expression for the intrinsic birefringence. Consider a photon wavevector of $\vec{q} = (1,1,0)/\sqrt{2}$. The dielectric impermeability tensor becomes

$$\begin{aligned} B_{11}(\vec{q}) &= 1/n^2 + q^2(P_{11} + P_{12})/2 \\ B_{22}(\vec{q}) &= 1/n^2 + q^2(P_{11} + P_{12})/2 \\ B_{33}(\vec{q}) &= 1/n^2 + q^2P_{12} \\ B_{32}(\vec{q}) &= 0 \\ B_{31}(\vec{q}) &= 0 \\ B_{21}(\vec{q}) &= q^2P_{44} \end{aligned} \quad (0.13)$$

The dielectric impermeability tensor is a 3x3 matrix with the form

$$\begin{bmatrix} a & c & 0 \\ c & a & 0 \\ 0 & 0 & b \end{bmatrix} \quad (0.14)$$

with eigenvalues and eigenvectors

$$\begin{aligned} & (1/n^2 + q^2[(P_{11} + P_{12})/2 + P_{44}]), \quad (1,1,0)/\sqrt{2} \\ & (1/n^2 + q^2[(P_{11} + P_{12})/2 - P_{44}]), \quad (-1,1,0)/\sqrt{2} . \\ & (1/n^2 + q^2 P_{12}), \quad (0,0,1) \end{aligned} \quad (0.15)$$

[0053] Light is traveling the same direction as the first eigenvector, so the second and third represent the principal axes for the index of refraction. Now, finally, we find different values of index to order q^2 for polarization along $\{-1,1,0\}$ and $\{0,0,1\}$:

$$\begin{aligned} \Delta n_{-1,1,0} &= -\frac{1}{2} n^3 [(P_{11} + P_{12})/2 - P_{44}] q^2 \\ \Delta n_{0,0,1} &= -\frac{1}{2} n^3 P_{12} q^2 \end{aligned} \quad (0.16)$$

Birefringence for light traveling in the $\{110\}$ direction has its maximum value at

$$BR = \Delta n_{-1,1,0} - \Delta n_{0,0,1} = -\frac{1}{2} n^3 [(P_{11} - P_{12})/2 - P_{44}] q^2 . \quad (0.17)$$

[0054] This is a very important equation. It gives the relation between tensor components and the largest intrinsic birefringence.

[0055] A glass, or any material that may be considered truly the same (on average) in every direction, has an even higher symmetry than a cubic crystal. In an isotropic material, a rank 4 tensor has only two independent components that may be taken as P_{11} and P_{12} . Isotropic materials obey the relation

$$P_{44} = (P_{11} - P_{12})/2 . \quad (0.18)$$

[0056] Since every direction is equivalent, we may consider light propagation in a $\langle 110 \rangle$ direction and look for a nonzero birefringence. Then Eq. (0.17) applies, but with Eq.(0.18), we see that $BR=0$. This had to be so, because we could just have easily considered $\langle 100 \rangle$ or $\langle 111 \rangle$ directions, where $BR=0$. Since all directions

are equivalent, the intrinsic birefringence must vanish in every direction. This is an important advantage for glasses.

Index of refraction vs. direction

[0057] Given an index ellipsoid or impermeability tensor B_{ij} , it is possible to define the indices of refraction for different polarizations and directions of light propagation. This is the kind of information needed for doing lens design or aberration modeling. The problem is more complicated for intrinsic birefringence, however, because the tensor B_{ij} itself changes for different directions of propagation, as shown above. Equation (0.6) gives all the information, but needs to be manipulated for each choice of directions given by q_1 , q_2 , and q_3 . Some simplifications should be possible. For example, for directions associated with rotating a vector in any plane equivalent to the xy plane, the direction goes through the sequence $[100]$, $[110]$, $[010]$, $[\bar{1}10]$, $[\bar{1}00]$, $[\bar{1}\bar{1}0]$, $[0\bar{1}0]$, $[1\bar{1}0]$, and then back to $[100]$ again. As these rotations are considered, the birefringence goes from 0 to its peak value given by Eq.(0.17) and back to 0 with 4 cycles, following the expression

$$BR = \left(-\frac{1}{2} n^3 [(P_{11} - P_{12})/2 - P_{44}] q^2 \right) \sin(2\theta) \quad (0.19)$$

where θ is the angle from the x-axis. It gets more complicated when the ray direction does not lie in a plane parallel to a cube face.

[0058] To estimate the intrinsic contribution to birefringence at various wavelengths, we consider only the direction of largest birefringence and take a value of 6.5 nm/cm at 157 nm. The expression to consider is Eq.(1.17), or

$$BR_{peak} = \left(-\frac{1}{2} n^3 [(P_{11} - P_{12})/2 - P_{44}] q^2 \right). \quad (0.20)$$

[0059] A Sellmeier expression for index variation of CaF_2 gives $n(157 \text{ nm})=1.5586$. To fit $BR = 6.5 \text{ nm/cm}$, and with $q = 2\pi/\lambda$, we deduce $[(P_{11} - P_{12})/2 - P_{44}] = 0.000214 \text{ nm}^2$. We expect these tensor components to have a little dispersion vs. wavelength, presumably getting smaller at longer wavelengths. As a result, the predicted intrinsic birefringence will be a little larger

than should actually be observed. Thus, keeping the tensor elements fixed in value from 157 nm but considering dispersion in index and q , the following table may be constructed:

| lambda(nm) | $q(1/\text{nm})$ | n | BR(nm/cm) |
|------------|------------------|----------|-----------|
| 147 | 0.042743 | 1.589 | 7.8 |
| 157 | 0.04002 | 1.5586 | 6.5 |
| 193 | 0.032555 | 1.5015 | 3.8 |
| 248 | 0.025335 | 1.468 | 2.2 |
| 253.65 | 0.024771 | 1.466 | 2.1 |
| 633 | 0.009926 | 1.432882 | 0.3 |

[0060] The intrinsic birefringence is 26 times larger at 147 nm than at 633 nm, of which 18 is due to $1/\lambda^2$ and the rest due to $q=0$ index variation. If these estimates are correct then intrinsic birefringence, viewed in a $\langle 110 \rangle$ direction, should be rather small at 633 nm but readily observable at 193 nm. Measured values gives 1.2 nm/cm at 253.65 nm, compared with estimate of 2.1, so the dispersion in the P constants makes the result by 633 nm even smaller.

[0061] To exhibit the complexity arising for directions off of $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$, consider a ray direction that stays in the xy plane but runs at some angle (e.g. between $\{100\}$ and $\{110\}$):

$$\vec{q} = (\cos(\theta), \sin(\theta), 0). \quad (0.21)$$

[0062] The eigenvectors for this case are not simply along \vec{q} and perpendicular to \vec{q} . It is important to point out that the ray direction in this case is not an eigenvector. In all the high symmetry cases considered previously, the ray direction was one of the eigenvectors (principal directions), but this is apparently not the case for a more general wavevector such as Eq.(0.21). In the special case in which we set $P_{44}=(P_{11}-P_{12})/2$, then the ray direction is always an eigenvector with eigenvalue $1/n^2+P_{11}q^2$ and the other eigenvectors are in the plane perpendicular to this, with degenerate eigenvalues $1/n^2+P_{12}q^2$. This merely reflects the consequences of being isotropic, as in a glass.

[0063] The eigenvalues for wavevector $\vec{q} = (\cos(\theta), \sin(\theta), 0)$ are given by

$$\begin{aligned}
 1/n_1^2 &= 1/n^2 + [(P_{11} + P_{12})/2 + R]q^2 \\
 1/n_2^2 &= 1/n^2 + [(P_{11} + P_{12})/2 - R]q^2 \\
 1/n_3^2 &= 1/n^2 + P_{12}q^2 \\
 R &= \frac{1}{2}[(P_{11} - P_{12})^2 \cos^2(2\theta) + (2P_{44})^2 \sin^2(2\theta)]^{\frac{1}{2}}
 \end{aligned}
 \tag{0.22}$$

[0064] This shows the explicit variation of indices of refraction with ray direction, but is hard to use until the in-plane eigenvector is calculated. (The other eigenvector is {001}.)

[0065] The invention provides optical elements formed from cubic fluoride crystals such as calcium fluoride, barium fluoride, strontium fluoride, and preferably CaF_2 , for use in short wavelength optical systems with light wavelengths below 194nm with the optical elements having a preferred 100 crystal orientation that minimizes intrinsic birefringence related to the short wavelength of the light transmitted through the crystal.

[0066] It will be apparent to those skilled in the art that various modifications and variations can be made to the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

We claim:

1. A method of making a <194 nm calcium fluoride crystal optical lithography element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence, said method comprising:
providing an optical element optical calcium fluoride crystal with an input face {100} crystal plane,
forming said input face {100} crystal plane into an optical lithography element surface of an optical lithography element having an optical axis, said optical axis aligned with a <100> crystal direction of said optical calcium fluoride crystal.
2. A method as claimed in claim 1 wherein forming includes forming said optical calcium fluoride crystal into a lens element with a curved optical element surface, said lens element having a lens optical axis aligned with a <100> crystal direction of said calcium fluoride crystal and normal to said {100} calcium fluoride crystal plane.
3. A method as claimed in claim 1 wherein forming includes forming said optical calcium fluoride crystal into a beam splitter cube with a beam splitter cube face parallel to said {100} calcium fluoride crystal plane and a beam splitter optical axis aligned with a <100> crystal direction of said calcium fluoride crystal.
4. A <194 nm calcium fluoride crystal optical lithography element for transmitting wavelengths less than 194 nm with minimal birefringence, said optical lithography element comprised of an optical calcium fluoride crystal with a {100} crystal plane and a <100> crystal direction, said optical element having an optical axis aligned with said <100> calcium fluoride crystal direction.
5. A method of making a fluoride crystal optical element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence, said method comprising:
providing an optical element optical fluoride crystal with an input face {100} crystal plane,

forming said input face {100} crystal plane into an optical element surface of an optical element having an optical axis, said optical axis aligned with a <100> crystal direction of said optical fluoride crystal.

6. A method as claimed in claim 5 wherein forming includes forming said optical fluoride crystal into a lens element with a curved optical element surface, said lens element having a lens optical axis aligned with a <100> crystal direction of said crystal and normal to said {100} crystal plane.

7. A method as claimed in claim 5 wherein forming includes forming said optical fluoride crystal into a beam splitter cube with a beam splitter cube face parallel to said {100} crystal plane and a beam splitter optical axis aligned with a <100> crystal direction of said crystal.

8. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of calcium.

9. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of barium.

10. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of strontium.

11. An optical element for transmitting wavelengths less than about 194 nm with minimal birefringence, said optical element comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction, said optical element having an optical axis aligned with said <100> crystal direction.

12. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of calcium .

$$\begin{aligned}
 1/n_1^2 &= 1/n^2 + [(P_{11} + P_{12})/2 + R]q^2 \\
 1/n_2^2 &= 1/n^2 + [(P_{11} + P_{12})/2 - R]q^2 \\
 1/n_3^2 &= 1/n^2 + P_{12}q^2 \\
 R &= \frac{1}{2} [(P_{11} - P_{12})^2 \cos^2(2\theta) + (2P_{44})^2 \sin^2(2\theta)]^{\frac{1}{2}}
 \end{aligned}
 \tag{0.22}$$

[0064] This shows the explicit variation of indices of refraction with ray direction, but is hard to use until the in-plane eigenvector is calculated. (The other eigenvector is {001}.)

[0065] The invention provides optical elements formed from cubic fluoride crystals such as calcium fluoride, barium fluoride, strontium fluoride, and preferably CaF_2 , for use in short wavelength optical systems with light wavelengths below 194nm with the optical elements having a preferred 100 crystal orientation that minimizes intrinsic birefringence related to the short wavelength of the light transmitted through the crystal.

[0066] It will be apparent to those skilled in the art that various modifications and variations can be made to the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

13. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of barium .
14. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of strontium .
15. An optical element as claimed in claim 11 wherein said optical element is a lens element with a curved optical element surface and a lens optical axis aligned with said $\langle 100 \rangle$ crystal direction.
16. An optical element as claimed in claim 11 wherein said optical element is a beam splitter cube with a beam splitter cube face parallel to said $\{100\}$ crystal plane and a beam splitter optical axis aligned with said $\langle 100 \rangle$ crystal direction.
17. A below 194 nm wavelength transmitting lens, said lens comprised of a cubic optical fluoride crystal with a $\{100\}$ crystal plane and a $\langle 100 \rangle$ crystal direction, said lens having a curved optical surface and an optical axis, said optical axis aligned with said $\langle 100 \rangle$ crystal direction and normal to said $\{100\}$ crystal plane.
18. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of calcium.
19. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of barium.
20. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of strontium.
21. A below 194 nm wavelength transmitting beam splitter cube, said beam splitter cube comprised of a cubic optical fluoride crystal with a $\{100\}$ crystal plane and a $\langle 100 \rangle$ crystal direction, said beam splitter cube having a beam splitter cube

face parallel to said {100} crystal plane and an optical axis aligned with said <100> crystal direction.

22. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of calcium.

23. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of barium.

24. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of strontium.

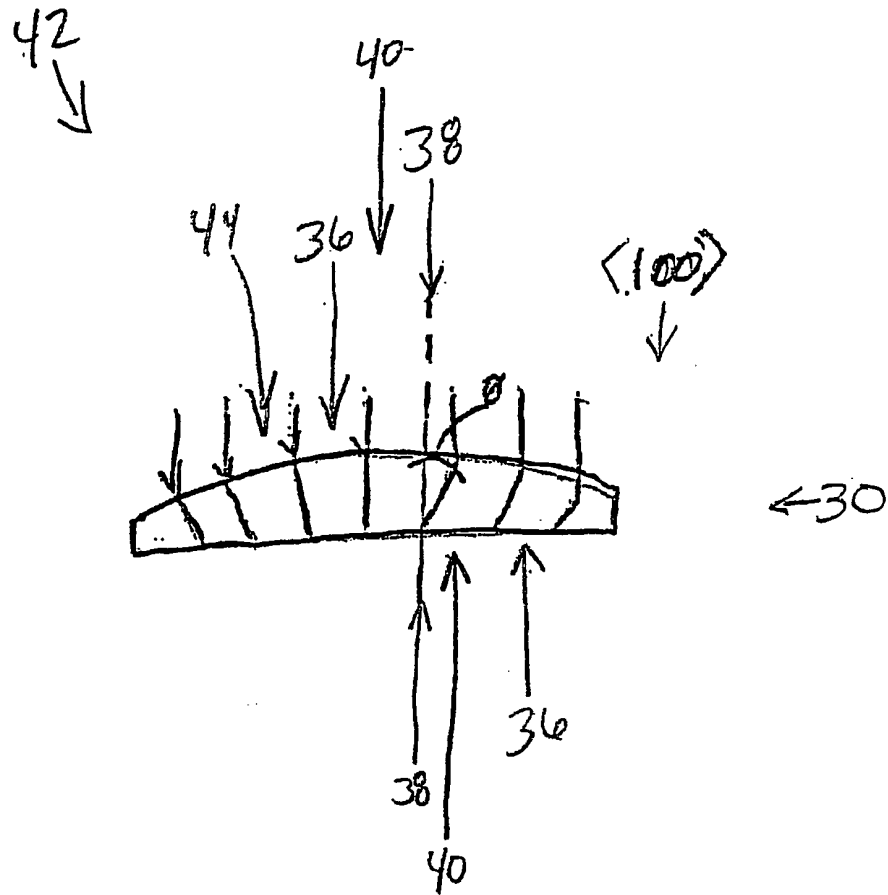


FIG. 1

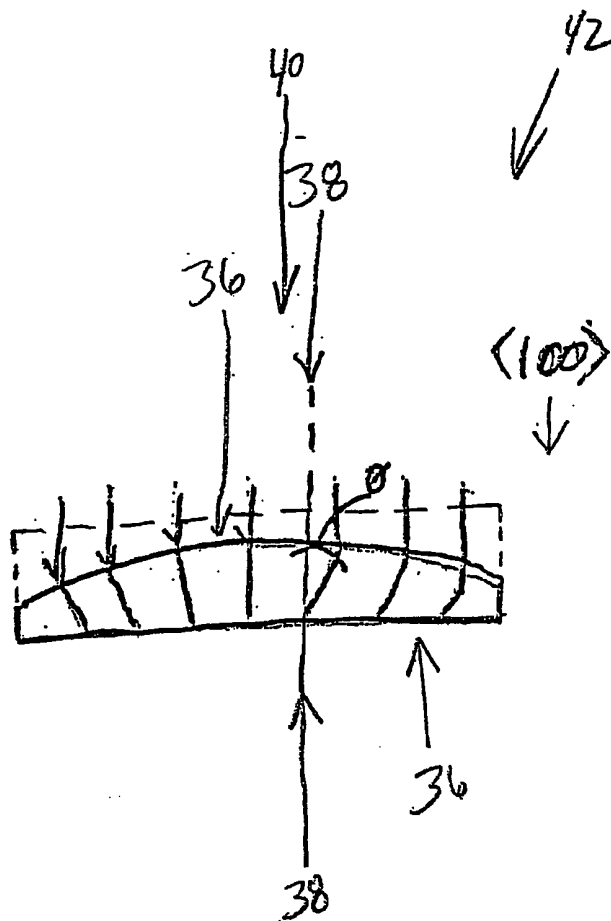


FIG. 1(a)

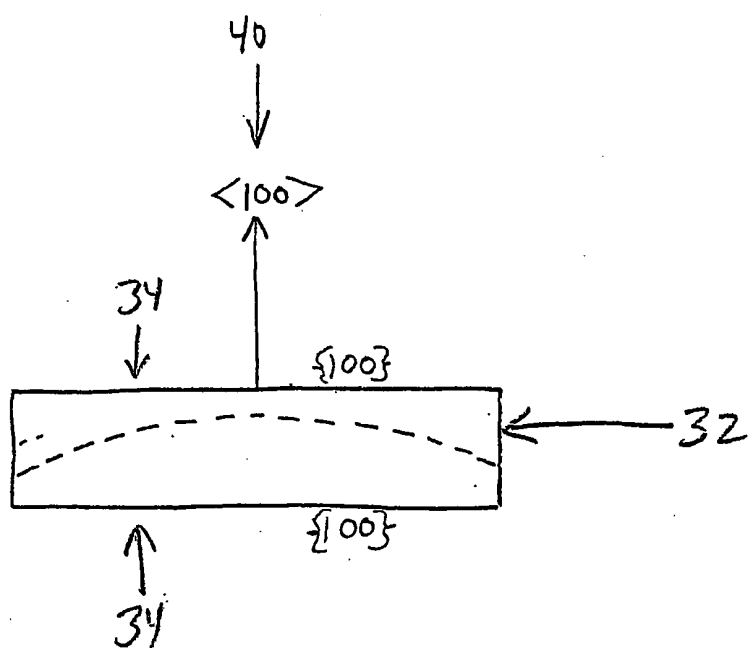
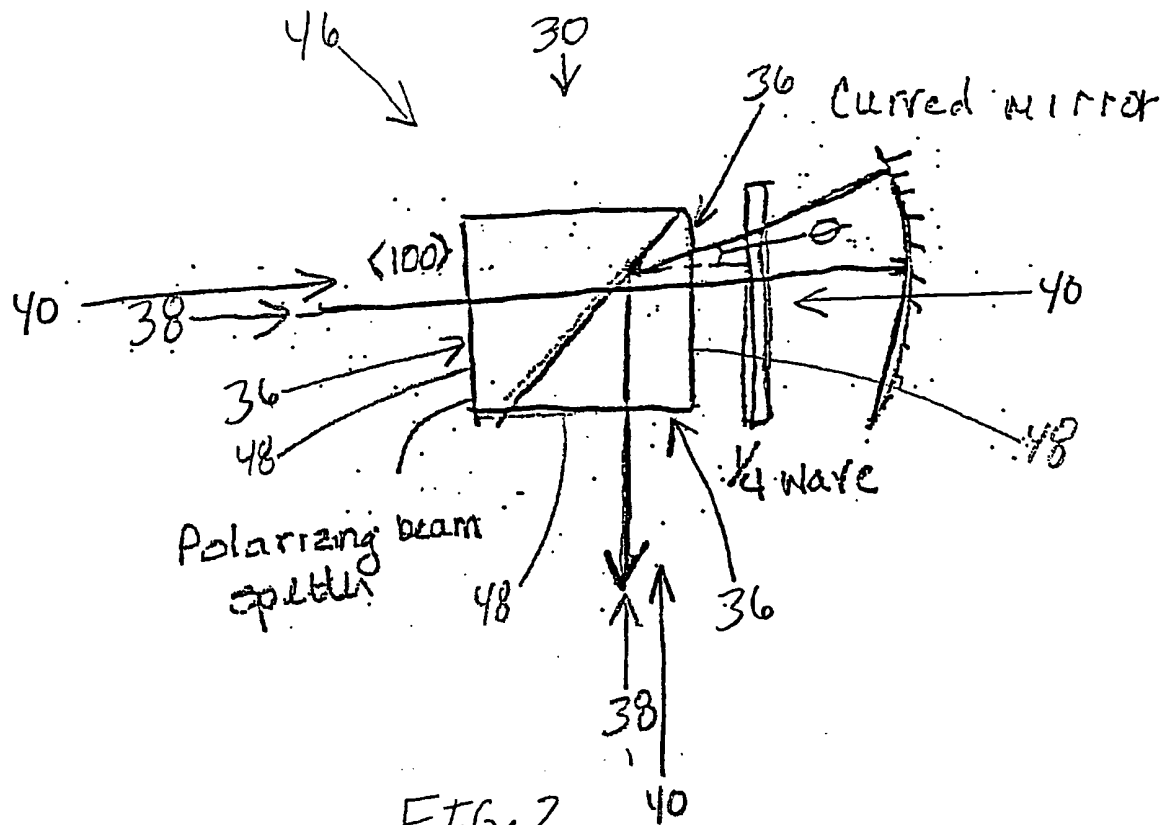


FIG. 1(b)



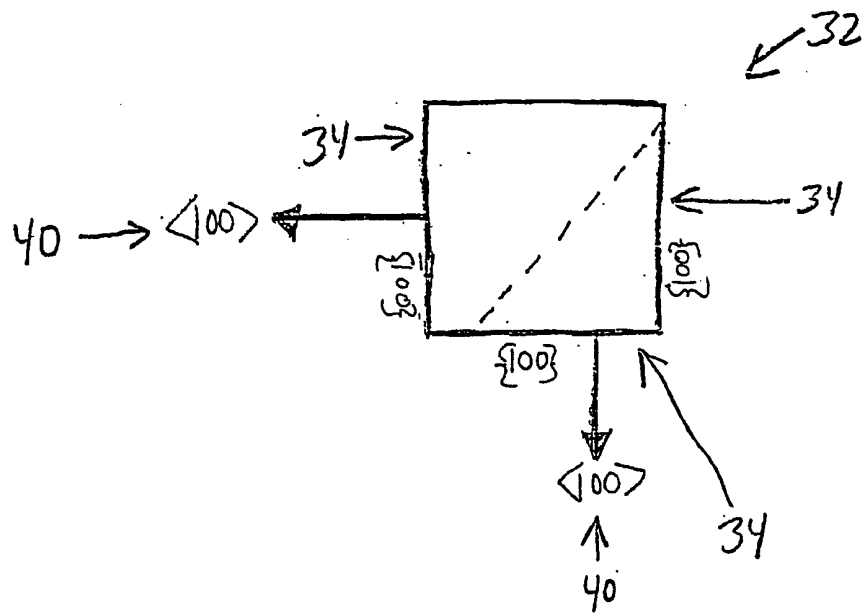
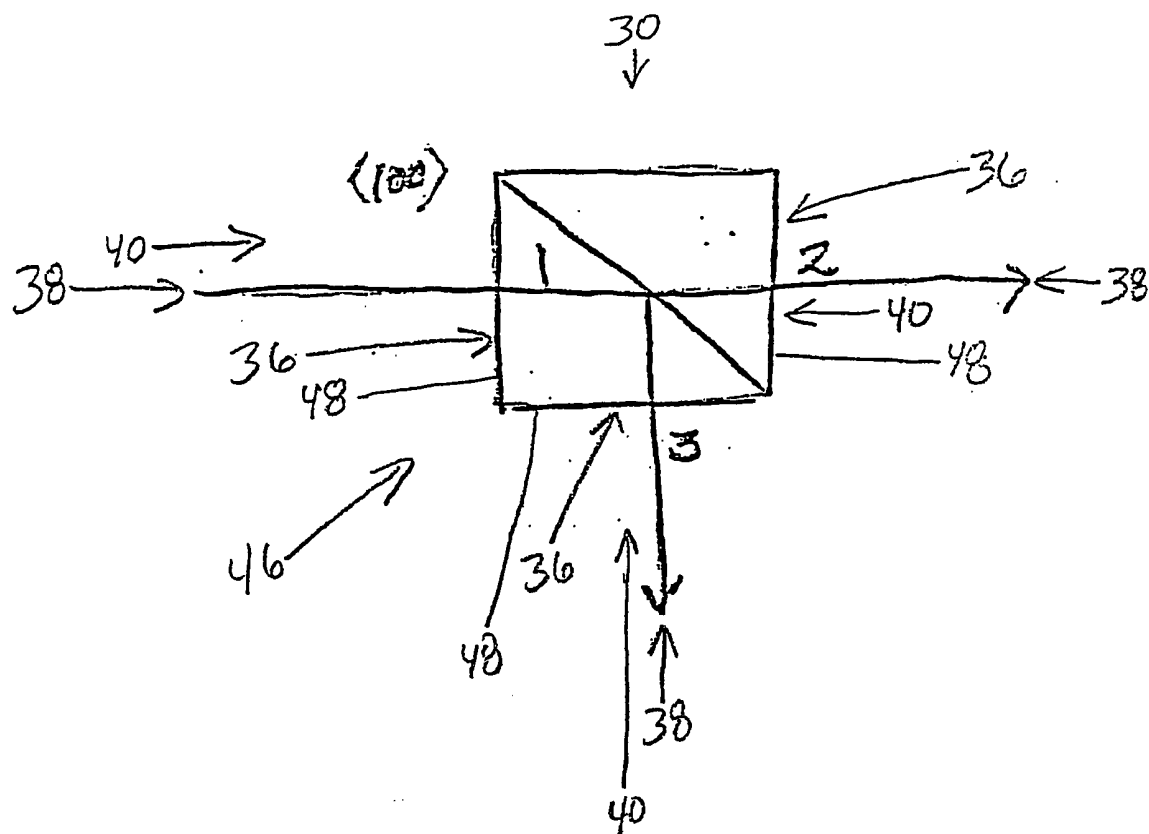


FIG. 2(a)



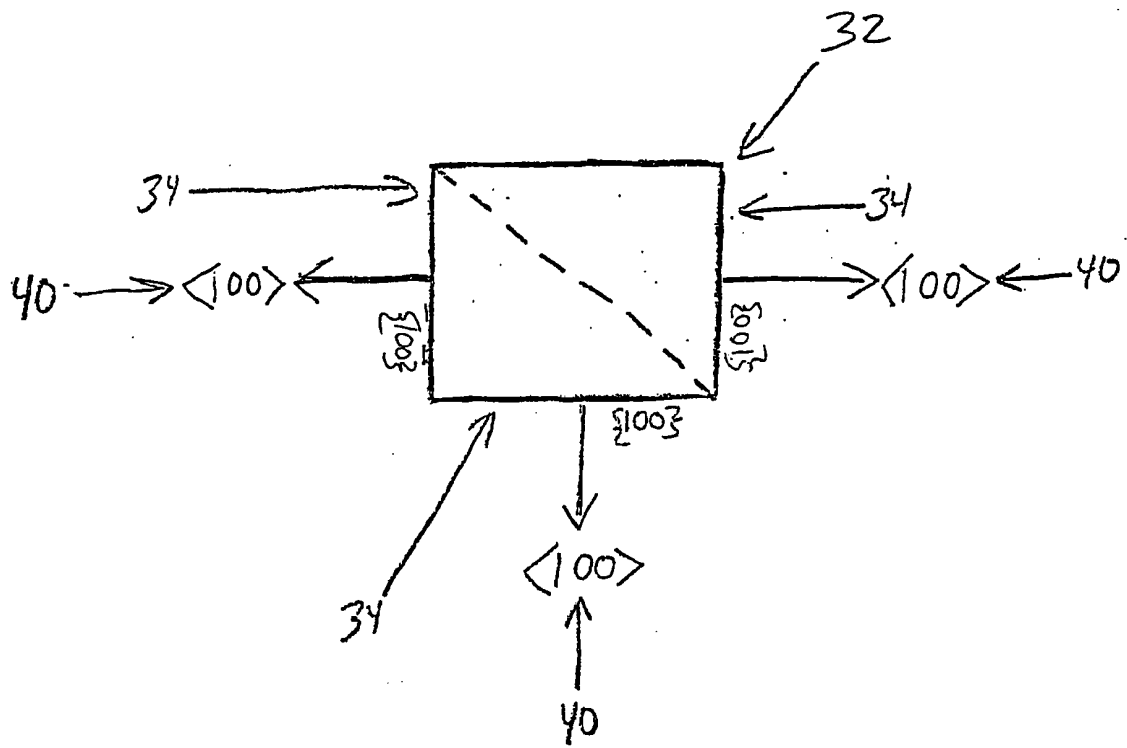


FIG. 3(a)

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(54) Title: PREFERRED CRYSTAL ORIENTATION OPTICAL ELEMENTS FROM CUBIC MATERIALS

(57) Abstract: The invention provides a method of making a <194 nm wavelength calcium fluoride crystal optical lithography element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence by providing an optical element optical calcium fluoride crystal with an input face {100} crystal plane and forming the input face {100} crystal plane into an optical lithography element surface of an optical lithography element having an optical axis, with the optical axis aligned with a <100> crystal direction of the optical calcium fluoride crystal. In a preferred embodiment, the below 194 nm transmitting optical element is a <100> oriented calcium fluoride lens. In a preferred embodiment, the below 194 nm transmitting optical element is a <100> oriented calcium fluoride beam splitter.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/15100

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : G02B 5/30, 13/14, 27/10, 27/12; F21V 9/06; G02F 1/01
US CL : 359/321, 322, 323, 350, 352, 355, 361, 618, 129, 634, 640

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | US 2001/0008540 A1 (OBA et al) 19 JULY 2000; page 1, sections 9, 10, 14, 19-21, 34 & 36; page 4, section 77 & 85; see figure 6. | 1-24 |
| X | US 6,201,634 B1 (SAKUMA et al) 13 MARCH 2001, column 1, lines 20-25, column 2, lines 10-19 & 65-67, col. 5, lines 40-50. | 1-24 |

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☐ See patent family annex.

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INTERNATIONAL SEARCH REPORT

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Continuation of B. FIELDS SEARCHED Item 3:

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(54) Title: **PREFERRED CRYSTAL ORIENTATION OPTICAL ELEMENTS FROM CUBIC MATERIALS**

(57) Abstract: The invention provides a method of making a <194 nm wavelength calcium fluoride crystal optical lithography element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence by providing an optical element optical calcium fluoride crystal with an input face {100} crystal plane and forming the input face {100} crystal plane into an optical lithography element surface of an optical lithography element having an optical axis, with the optical axis aligned with a <100> crystal direction of the optical calcium fluoride crystal. In a preferred embodiment, the below 194 nm transmitting optical element is a <100> oriented calcium fluoride lens. In a preferred embodiment, the below 194 nm transmitting optical element is a <100> oriented calcium fluoride beam splitter.

AMENDED CLAIMS

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We claim:

1. A method of making a <194 nm calcium fluoride crystal optical lithography element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence, said method comprising:
 - providing an optical element optical calcium fluoride crystal with an input face {100} crystal plane,
 - forming said input face {100} crystal plane into an optical lithography element surface of an optical lithography element having an optical axis, said optical axis aligned with a <100> crystal direction of said optical calcium fluoride crystal,
 - wherein said formed optical lithography element having an optical axis aligned with a <100> crystal direction is used in an optical lithography system for transmitting wavelengths <194nm.
2. A method as claimed in claim 1 wherein forming includes forming said optical calcium fluoride crystal into a lens element with a curved optical element surface, said lens element having a lens optical axis aligned with a <100> crystal direction of said calcium fluoride crystal and normal to said {100} calcium fluoride crystal plane.
3. A method as claimed in claim 1 wherein forming includes forming said optical calcium fluoride crystal into a beam splitter cube with a beam splitter cube face parallel to said {100} calcium fluoride crystal plane and a beam splitter optical axis aligned with a <100> crystal direction of said calcium fluoride crystal.
4. A <194 nm calcium fluoride crystal optical lithography element for transmitting wavelengths less than 194 nm with minimal birefringence, said optical lithography element comprised of an optical calcium fluoride crystal with a {100} crystal plane and a <100> crystal direction, said optical element having an optical axis aligned with said <100> calcium fluoride crystal direction.

5. A method of making a fluoride crystal optical element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence, said method comprising:

providing an optical element optical fluoride crystal with an input face {100} crystal plane,

forming said input face {100} crystal plane into an optical element surface of an optical element having an optical axis, said optical axis aligned with a <100> crystal direction of said optical fluoride crystal,

wherein said fluoride crystal element transmits wavelengths <194nm along an optical axis aligned with a <100> crystal direction of said optical fluoride crystal.

6. A method as claimed in claim 5 wherein forming includes forming said optical fluoride crystal into a lens element with a curved optical element surface, said lens element having a lens optical axis aligned with a <100> crystal direction of said crystal and normal to said {100} crystal plane.

7. A method as claimed in claim 5 wherein forming includes forming said optical fluoride crystal into a beam splitter cube with a beam splitter cube face parallel to said {100} crystal plane and a beam splitter optical axis aligned with a <100> crystal direction of said crystal.

8. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of calcium.

9. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of barium.

10. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of strontium.

11. An optical element for transmitting wavelengths less than about 194 nm with minimal birefringence, said optical element comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction, said optical element having an optical axis aligned with said <100> crystal direction,
wherein said optical element having an optical axis aligned with said <100> crystal direction transmits <194nm wavelengths.
12. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of calcium.
13. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of barium.
14. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of strontium.
15. An optical element as claimed in claim 11 wherein said optical element is a lens element with a curved optical element surface and a lens optical axis aligned with said <100> crystal direction.
16. An optical element as claimed in claim 11 wherein said optical element is a beam splitter cube with a beam splitter cube face parallel to said {100} crystal plane and a beam splitter optical axis aligned with said <100> crystal direction.
17. A below 194 nm wavelength transmitting lens, said lens comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction, said lens having a curved optical surface and an optical axis, said optical axis aligned with said <100> crystal direction and normal to said {100} crystal plane,
wherein said lens having an optical axis aligned with said <100> crystal direction and normal to said {100} crystal plane transmits <194nm wavelengths.

18. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of calcium.
19. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of barium.
20. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of strontium.
21. A below 194 nm wavelength transmitting beam splitter cube, said beam splitter cube comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction, said beam splitter cube having a beam splitter cube face parallel to said {100} crystal plane and an optical axis aligned with said <100> crystal direction.
22. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of calcium.
23. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of barium.
24. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of strontium.

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(57) Abstract: The invention provides a method of making a <194 nm wavelength calcium fluoride crystal optical lithography element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence by providing an optical element optical calcium fluoride crystal with an input face {100} crystal plane and forming the input face {100} crystal plane into an optical lithography element surface of an optical lithography element having an optical axis, with the optical axis aligned with a <100> crystal direction of the optical calcium fluoride crystal. In a preferred embodiment, the below 194 nm transmitting optical element is a <100> oriented calcium fluoride lens. In a preferred embodiment, the below 194 nm transmitting optical element is a <100> oriented calcium fluoride beam splitter.

PREFERRED CRYSTAL ORIENTATION OPTICAL ELEMENTS FROM CUBIC MATERIALS

[0001] This application claims the benefit of, and incorporates by reference, U. S. Provisional Application, 60/291,424 filed May 16, 2001 by N.F. Borrelli, D.C. Allan, C.M. Smith, and B.D. Stone entitled PREFERRED CRYSTAL ORIENTATION OPTICAL ELEMENTS FROM CUBIC MATERIALS.

FIELD OF THE INVENTION

[0002] The present invention relates generally to short wavelength optical systems and elements for use therein, optical projection lithography methods and photolithography, and particularly to optical photolithography fluoride crystal elements for use in optical photolithography systems and short wavelength optical systems utilizing ultraviolet light (UV) wavelengths below 194 nm, such as UV lithography systems utilizing wavelengths in the 193 nm region and the 157 nm region.

TECHNICAL BACKGROUND

[0003] Projection optical photolithography methods/systems that utilize the ultraviolet wavelengths of light below 194 nm provide benefits in terms of achieving smaller feature dimensions. Such methods/systems that utilize ultraviolet wavelengths in the 157 nm and the 193 nm wavelength regions have the potential of improving the manufacturing of integrated circuits with smaller feature sizes but the commercial use and adoption of below 194 nm UV in high volume mass production of integrated circuits has been slow. Part of the slow progression to below 194 nm UV by the semiconductor industry has been due to the lack of economically manufacturable fluoride cubic crystal optical elements with high performance at such short wavelengths. For the benefit of ultraviolet photolithography in the 157 nm region such as the emission spectrum window of a fluorine excimer laser and the 193 nm region such as the ArF excimer laser emission spectrum to be utilized in the manufacturing of integrated circuits there is a need for fluoride crystal optical

elements that have beneficial optical properties and that can be designed for and utilized with below 194nm UV photons. The Argon Fluoride emits at ~193 nm and the Fluorine (F₂) excimer emits at ~157 nm, and for various optical applications it is preferable to have such short wavelengths of light less than 194 nm. For use with optical systems with Fluorine (F₂) lasers or Argon Fluoride lasers, the preferred crystal material for optical elements has been calcium fluoride, a cubic fluoride crystal.

SUMMARY

[0004] The invention includes a method of making a < 194 nm wavelength transmitting calcium fluoride crystal optical lithography element for transmitting wavelengths less than about 194 nm along an optical axis with minimal intrinsic birefringence. The method includes providing an optical element calcium fluoride crystal with an input face {100} crystal plane and forming said input face {100} crystal plane into an optical lithography element surface of an optical lithography element having an optical axis, with the optical axis aligned with a <100> crystal direction of the calcium fluoride crystal.

[0005] The invention includes a <194 nm wavelength transmitting calcium fluoride crystal optical lithography element for transmitting wavelengths less than 194 nm with minimal intrinsic birefringence. The optical lithography element is comprised of an optical calcium fluoride crystal with a {100} crystal plane and a <100> crystal direction with the optical element having an optical axis aligned with the <100> calcium fluoride crystal direction.

[0006] The invention includes a method of making a fluoride crystal optical element for transmitting short wavelengths of light (<194 nm) along an optical axis with minimal intrinsic birefringence. The method includes providing an optical element optical fluoride crystal with an input face {100} crystal plane and forming the input face {100} crystal plane into an optical element surface of an optical element having an optical axis with the optical axis aligned with a <100> crystal direction of the optical fluoride crystal.

[0007] The invention includes an optical element for transmitting wavelengths less than about 194 nm with minimal intrinsic birefringence. The optical element is comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction with the optical element having an optical axis aligned with the <100> crystal direction.

[0008] The invention includes a below 194 nm wavelength transmitting lens with minimal intrinsic birefringence comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction. The lens has a curved optical surface and an optical axis aligned with the <100> crystal direction and normal to the {100} crystal plane.

[0009] The invention includes a below 194 nm wavelength transmitting beam splitter cube with minimal intrinsic birefringence. The beam splitter cube is comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction with the beam splitter cube face parallel to the {100} crystal plane and an optical axis aligned with the <100> crystal direction.

[0010] Additional features and advantages of the invention will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the invention as described in the written description and claims hereof, as well as the appended drawings.

[0011] It is to be understood that both the foregoing general description and the following detailed description are merely exemplary of the invention, and are intended to provide an overview or framework to understanding the nature and character of the invention as it is claimed.

[0012] The accompanying drawings are included to provide a further understanding of the invention, and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiment(s) of the invention, and together with the description serve to explain the principles and operation of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1, 1(a) and 1(b) show an embodiment of the invention with a $\langle 100 \rangle$ crystal direction oriented fluoride crystal lens element.

[0014] FIG. 2 and 2(a) show an embodiment of the invention with a $\langle 100 \rangle$ crystal direction oriented fluoride crystal beam splitter element.

[0015] FIG. 3 and 3(a) show an embodiment of the invention with a $\langle 100 \rangle$ crystal direction oriented fluoride crystal beam splitter element.

DETAILED DESCRIPTION

[0016] The invention includes a method of making a $\langle 194 \text{ nm} \rangle$ wavelength transmitting calcium fluoride crystal optical lithography element 30 for transmitting wavelengths less than about 194 nm, such as 193 nm or 157 nm, along an optical axis with minimal birefringence. The method includes providing an optical element optical calcium fluoride crystal 32 with an input face $\{100\}$ crystal plane 34. The method includes forming the input face $\{100\}$ crystal plane 34 into an optical lithography element surface 36 of the optical lithography element 30 having an optical axis 38 with the optical axis 38 aligned with a $\langle 100 \rangle$ crystal direction 40 of the optical calcium fluoride crystal 32. In an embodiment, forming includes forming the calcium fluoride crystal 32 into a lens element 42 with a curved optical element surface 44. The formed lens element 42 having a lens optical axis 38 aligned with a $\langle 100 \rangle$ crystal direction 40 of the calcium fluoride crystal and normal to the $\{100\}$ calcium fluoride crystal plane 34. In an embodiment, forming includes forming the optical calcium fluoride crystal 32 into a beam splitter cube 46 with a beam splitter cube face 48 parallel to the $\{100\}$ calcium fluoride crystal plane 34 and a beam splitter optical axis 38 aligned with a $\langle 100 \rangle$ crystal direction 40 of crystal 32.

[0017] The invention includes a $\langle 194 \text{ nm} \rangle$ wavelength calcium fluoride crystal optical lithography element 30 for transmitting wavelengths less than 194 nm with minimal intrinsic birefringence. The optical lithography element 30 is comprised of an optical calcium fluoride crystal 32 with a $\{100\}$ crystal plane 34 and a $\langle 100 \rangle$ crystal direction 40. The optical element has an optical axis 38 aligned with the $\langle 100 \rangle$ calcium fluoride crystal direction 40. The optical element surface of the element is preferably normal to the optical axis 38, with the optical surface formed in

alignment with the crystals {100} crystal plane. In an embodiment the calcium fluoride crystal optical element is a lens. In an embodiment the calcium fluoride crystal optical element is a beam splitter.

[0018] The invention includes a method of making a fluoride crystal optical element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence. Preferably the method includes making a cubic fluoride crystal optical lithography element for lithography systems that operate at less than 194 nm, such as 193 wavelengths or 157 nm wavelengths. The method includes providing an optical element optical fluoride crystal 32 with an input face {100} crystal plane 34 and forming the face {100} plane into an optical element surface 36 of an optical element 30 having an optical axis 38 aligned with a <100> crystal direction 40 of the optical fluoride crystal 32. In an embodiment, forming includes forming the optical fluoride crystal 32 into a lens element 42 with a curved optical element surface 44, with the lens element 42 having a lens optical axis 38 aligned with a <100> crystal direction 40 of crystal 32 and normal to the {100} crystal plane 34 of crystal 32. In a preferred embodiment crystal 32 is formed into a lens element 42 for directing a cone of light rays having a cone angle θ of at least 35.26°. In another embodiment, crystal 32 is formed into a beam splitter cube 46 with a beam splitter cube face 48 parallel to the {100} crystal plane 34 and a beam splitter optical axis 38 aligned with a <100> crystal direction 40 of crystal 32. In a preferred embodiment the crystal 32 is formed into a beam splitter cube for use with a curved mirror to deliver a polarized light having a <194 nm wavelength, with incoming light rays incident at an angle onto the cube. In a preferred embodiment the crystal 32 is formed into an interferometry beam splitter cube for use below 194 nm light rays, with light rays travelling along the optical axis in alignment with the <100> directions ([100], [010], [001]) of crystal 32. In a preferred embodiment crystal 32 is formed into an optical element 30 with minimized intrinsic birefringence with element for use in below 194 nm optical applications when light through the optical element is not perpendicular to the {100} crystal planes. In an embodiment optical fluoride crystal 32 is comprised of calcium, preferably comprised of calcium fluoride and most preferably consists essentially of CaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment optical fluoride crystal 32 is comprised of

barium, preferably comprised of barium fluoride, and most preferably consists essentially of BaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment optical fluoride crystal 32 is comprised of strontium, preferably comprised of strontium fluoride, and most preferably consists essentially of SrF_2 with a below 194 nm internal transmission of at least 99%/cm.

[0019] The invention includes an optical element for transmitting wavelengths less than about 194 nm with minimal intrinsic birefringence. The optical element is comprised of a cubic optical fluoride crystal with a {100} crystal plane and a $\langle 100 \rangle$ crystal direction with the optical element having an optical axis aligned with the $\langle 100 \rangle$ crystal direction. In a preferred embodiment, the element is a below 194 nm lithography element for transmitting a below 194 nm lithography wavelength such as a 193 nm wavelength or a 157 nm wavelength in an optical lithography system. The optical element 30 transmits below 194 nm light along an optical axis 38. The optical element 30 is comprised of a cubic optical fluoride crystal 32 with a {100} crystal plane 34 and a $\langle 100 \rangle$ crystal direction 40, with the optical axis 38 aligned with a $\langle 100 \rangle$ crystal direction 40 and normal to a {100} crystal plane 34. The optical element 30 has an optical element surface 36 that is aligned with a {100} crystal plane and normal to a $\langle 100 \rangle$ crystal direction optical axis of the element. In an embodiment the optical fluoride crystal 32 of element 30 is comprised of calcium, preferably calcium fluoride, and most preferably the crystal consists essentially of CaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the optical fluoride crystal 32 of element 30 is comprised of barium, preferably barium fluoride, and most preferably the crystal consists essentially of BaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the optical fluoride crystal 32 of element 30 is comprised of strontium, preferably strontium fluoride and most preferably the crystal consists essentially of SrF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment optical element 30 is a lens element with a curved optical surface and a lens optical axis 38 aligned with the $\langle 100 \rangle$ crystal direction. Preferably the lens element has a cone angle θ for a cone of light rays with the cone angle at least 35.26° , with the light rays not perpendicular to the {100} crystal planes. In an embodiment optical element 30 is a beam splitter cube with a beam splitter cube

face 48 parallel to the {100} crystal plane and a beam splitter optical axis aligned with the $\langle 100 \rangle$ crystal direction. In a preferred embodiment the beam splitter cube is a lithography element for use with the curved mirror to deliver a polarized light having a <194 nm wavelength, preferably with incoming light rays incident at an angle onto the cube. In a preferred embodiment, the beam splitter cube is an interferometry beam splitter cube for use with below 194 nm light rays with light rays travelling along the optical axis in alignment with the $\langle 100 \rangle$ crystal directions. The optical element 30 provides for minimized intrinsic birefringence at short wavelengths below 194 nm.

[0020] The invention includes a below 194 nm wavelength transmitting lens 42 comprised of a cubic optical fluoride crystal with a {100} crystal plane and a $\langle 100 \rangle$ crystal direction with the lens having a curved optical surface 44 and an optical axis 38. The lens optical axis 38 is aligned with the $\langle 100 \rangle$ crystal direction and normal to the {100} crystal plane. In a preferred embodiment the below 194 nm transmitting lens optical fluoride crystal is comprised of calcium, preferably calcium fluoride and most preferably consists essentially of CaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the below 194 nm transmitting lens optical fluoride crystal is comprised of barium, preferably barium fluoride, most preferably the crystal consists essentially of BaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the below 194 nm transmitting lens optical fluoride crystal is comprised of strontium, preferably strontium fluoride crystal, and most preferably the crystal consists essentially of SrF_2 with a below 194 nm internal transmission of at least 99%/cm. Preferably the lens element has a cone angle θ for a cone of light rays with the cone angle at least 35.26° . Preferably the optical element crystal lens provides for minimized intrinsic birefringence at short wavelength light rays below 194 nm that are non perpendicular to the {100} crystal plane 34.

[0021] The invention includes a below 194 nm wavelength transmitting beam splitter cube 46 comprised of a cubic optical fluoride crystal with a {100} crystal plane and a $\langle 100 \rangle$ crystal direction with the beam splitter cube having a beam splitter cube face 48 parallel to the {100} crystal plane and having a beam splitter optical axis aligned with the $\langle 100 \rangle$ crystal direction. In a preferred embodiment the below 194

nm beam splitter cube optical fluoride cubic crystal is comprised of calcium, preferably calcium fluoride, and most preferably the cubic crystal consists essentially of CaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the below 194 nm beam splitter cube optical fluoride cubic crystal is comprised of barium, preferably barium fluoride and most preferably consists essentially of BaF_2 with a below 194 nm internal transmission of at least 99%/cm. In an embodiment the below 194 nm beam splitter cube optical fluoride cubic crystal is comprised of strontium, preferably strontium fluoride and most preferably consists essentially of SrF_2 with a below 194 nm internal transmission of at least 99%/cm. In a preferred embodiment the beam splitter cube 46 is a lithography element for use with lithography wavelengths such as 193 or 157 nm. Preferably the lithography element beam splitter is for use with a curved mirror to deliver a polarized light having a <194 nm wavelength preferably with incoming light rays incident at an angle onto a cube face 48. In a preferred embodiment the beam splitter cube 46 is a interferometry optical element for use with below 194 nm light rays with light rays travelling along the axis aligned with a <100> direction of the crystal. The beam splitter cube optical element 46 provides for minimizing intrinsic birefringence at short wavelengths below 194 nm by utilizing the <100> crystal directions of the cubic fluoride crystal 32.

[0022] Up until now the concern with cubic crystals with respect to birefringence has been related to that associated with stress birefringence, as a consequence of the growth process. This has pointed to a preferred direction for use the crystals with the incident plane being {111}, the plane where the effect of the stress birefringence is minimized.

[0023] However there is an intrinsic birefringence in cubic crystals that has not been considered. This birefringence has nothing to do with stress. The intrinsic birefringence becomes comparable to the stress birefringence at shorter wavelengths. Intuition suggests that cubic crystalline materials, such as CaF_2 or BaF_2 , are optically isotropic. In other words, the index of refraction or dielectric tensor is the same for light propagation in any arbitrary direction. In this way, cubic crystals resemble glasses, with isotropic optical properties. For cubic crystals it turns out that this picture is only valid in the limit in which the light wavelength is very long

compared with interatomic dimensions. As the material is used at shorter wavelengths additional contributions to the optical response are no longer negligible. These additional contributions create a directionally dependent index of refraction, i.e. intrinsic birefringence. It is important to note that this birefringence is not stress-related birefringence. It is an intrinsic property of any cubic crystal and is not removable by annealing.

[0024] It is shown that this intrinsic birefringence vanishes for light propagating in the symmetry directions $\langle 111 \rangle$ or $\langle 100 \rangle$, but reaches its maximum value for light going in the $\langle 110 \rangle$ directions.

[0025] It has been the practice to fabricate optics of CaF_2 by using the $\{111\}$ crystal plane to form the input face of the optic. The fabrication of an optic where light will be propagating through it in directions other than normal to the $\{111\}$ plane (or equivalently high symmetry directions) presents a case where the intrinsic birefringence described here could be an issue.

[0026] Three examples are shown in the attached FIGs. The first two examples are related to imaging applications at short wavelengths. The first case is where the optic itself has curvature (FIG. 1). Consider an example case that includes a cone of light rays at an angle θ of at least $\cos^{-1}(2/6^{1/2}) = 35.26$ degrees. In that cone $\langle 110 \rangle$ directions are included and peak birefringence should be observed at several locations. Of the 12 equivalent $\langle 110 \rangle$ directions only 3 lie within less than 90 degrees of $[111]$. These are $[110]$, $[101]$ and $[011]$. Since the cone of light includes these three directions, three equivalent peaks in birefringence should be observed 120 degrees apart in the transmitted intensity. If one considers a similar case except now using the $\{100\}$ plane as the incident face, it can be shown that the cone of incidence sweeps a larger angle for the same birefringence. Alternatively expressed, the same cone angle has less birefringence when the $\{100\}$ plane is used.

[0027] The second example is where one would use a curved mirror in association with a flat cube beam splitter (FIG. 2) to deliver polarized light. A quarter wave plate is also included in this design. In this case, due to the reflection from the curved mirror, the incoming rays are incident at an angle onto the cube. This is a

related situation to that shown in Figure 1 and here again the {100} face should offer an advantage in minimizing inherent birefringence.

[0028] Finally, interferometry applications that utilize calcium fluoride would also benefit from the recognition of the utility of the {100} plane. A schematic of this is shown in FIG. 3. If ray 1 travels in the $\langle 111 \rangle$ direction, then it experiences no intrinsic birefringence. However, in this case, ray 3 must travel in one of the $\langle 110 \rangle$ directions because these are at right angles to the $\langle 111 \rangle$ direction, experiencing maximum intrinsic birefringence.

[0029] Alternatively, if ray 1 travels in the $\langle 100 \rangle$ direction of the crystal, then ray 3 can travel in the $\langle 010 \rangle$ direction. Both of these directions have zero intrinsic birefringence. This approach would negate the use of a waveplate in the interferometer design.

[0030] The relevance of using the orientation that minimizes the amount of intrinsic birefringence encountered is in applications where wavefront integrity is critical. That would include short wavelength lithography and interferometry functions.

[0031] Intrinsic birefringence is zero in the {111} and {100} planes of cubic crystals and maximized in the {110} plane. It is proposed that the {100} plane is preferable for minimizing the effects of inherent birefringence, particularly when light through the optic is not perpendicular to the crystal plane.

[0032] In FIG. 3, with the cube beam splitter, light enters along path 1 and is split into paths 2 and 3 with equal path length through material. Intrinsic birefringence is zero in the $\langle 111 \rangle$ directions and zero in $\langle 111 \rangle$ and $\langle 100 \rangle$ directions. To avoid the effects of the naturally occurring birefringence, we fabricate a cubic optic such that the {100} face (or equivalent) of the crystal is the input face of the optic. In this case, ray 3 shown in FIG. 3 will emerge from the {010} face or equivalent of {100}. Thus the incident, transmitted, and reflected rays of FIG. 3 will experience no intrinsic birefringence.

[0033] This describes a simple physical picture of intrinsic birefringence of CaF_2 and other cubic crystals and also mathematical analysis of an intrinsic birefringence in cubic crystals that is only observable at short wavelength.

[0034] Ordinarily, cubic crystals such as CaF_2 are considered to have negligible intrinsic birefringence because of their cubic symmetry. (We are not considering birefringence induced by residual stresses.) However, as the light wavelength decreases, light waves experience a slightly different environment for different directions of propagation. Quantitatively, this effect is manifested as an additional symmetry-breaking term giving rise to intrinsic birefringence that is proportional to the inverse square of wavelength. This level of birefringence can be detrimental to optical performance at 157 nm and 193 nm.

[0035] The symmetry-breaking term proportional to $1/\lambda^2$, discussed is expected to occur in cubic systems from fundamental principles. Likewise, this term is absent from completely isotropic materials like glasses. The intrinsic birefringence vanishes for certain high symmetry directions of propagation, like $\langle 111 \rangle$ and $\langle 100 \rangle$, and reaches its maximum value for the in-between directions $\langle 110 \rangle$. Thus, for example, light traveling down a typical optic axis in the $\langle 111 \rangle$ direction will experience no intrinsic birefringence.

[0036] There is a rough estimate of the size of the intrinsic value, due to H. A. Lorentz, Collected Papers III, page 314:

$$\Delta n = 0.44\pi n(n^2 - 1)^2 (a / \lambda)^2 \quad (0.1)$$

where Δn is the birefringence, n is the index of refraction, "a" is a characteristic length that may be taken as a typical bond length, and λ is the wavelength of light. To get an estimate for $\lambda = 147\text{nm}$, take a literature value of $n=1.589$ and a bond length of 0.2365 nm for CaF_2 to get $\lambda n = 13 \times 10^{-6}$ or 130 nm/cm. The Lorentz estimate is believed to be on the high side by about a factor of 5. Consider this a very rough approximation with the correct $1/\lambda^2$ dependence.

[0037] To appreciate why the effect is largest in $\langle 110 \rangle$ directions and vanishes in $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, it suffices to consider the symmetries of a cube. If you look down an x, y, or z axis of a cube (i.e. $\langle 100 \rangle$ direction), you find that a 4-fold rotation carries the cube back into coincidence. Similarly, if you look down a body diagonal (i.e. $\langle 111 \rangle$ direction), you find a 3-fold symmetry rotation. Either of these symmetry rotations is enough to mix the components of any two-dimensional vector lying in the plane perpendicular to the rotation axis, destroying any birefringence for light waves traveling straight down either axis. If you look down the

cube in a $\langle 110 \rangle$ direction (e.g. looking down a line that runs across a cube face), you see an obviously rectangular symmetry that has only a 2-fold rotational symmetry. A 2-fold rotation does not mix vector components, so birefringence is possible. This turns out to be the direction of highest birefringence.

[0038] Before jumping into the mathematics, consider one more picture for light cone birefringence. With a cone of light whose average direction is $\langle 111 \rangle$; if the cone includes rays at an angle of at least $\cos^{-1}(\frac{2}{\sqrt{6}}) = 35.26^\circ$ (designs can reach 42° in the CaF_2), then $\langle 110 \rangle$ directions are included and peak birefringence should be observed at several locations. Of the 12 equivalent $\langle 110 \rangle$ directions, only three lie within less than 90° of $\langle 111 \rangle$. These are $[110]$, $[101]$, and $[011]$. Since the cone of light includes these three directions, three equivalent peaks in birefringence should be observed 120° apart in the transmitted intensity.

[0039] This section of mathematical details starts with the fundamental expression for the dielectric tensor, that is derivable from first principles, and derives several important expressions and results. This section is important to prove the vanishing of the intrinsic birefringence along $\langle 100 \rangle$ and $\langle 111 \rangle$, to show the vanishing of the intrinsic birefringence in isotropic materials (a kind of check on the algebra), and to show the nonzero result for the $\langle 110 \rangle$ directions. For light in the $\langle 110 \rangle$ direction, the detailed analysis also provides the directions of the principal optic axes.

[0040] The general expression for the dielectric tensor, including nonzero photon wavevector \vec{q} , is

$$\varepsilon_{\mu\nu}(\vec{q}) = \varepsilon_{\mu\nu}(\vec{q} = 0) + R_{\mu\nu ij} q_i q_j \quad (0.2)$$

where $R_{\mu\nu ij}$ is a new rank 4 tensor that accounts for the influence of nonzero wavevector on ε . This expression is derivable from fundamental quantum mechanics for optical response. Most conventional derivations take the $\vec{q} \rightarrow 0$ limit because that is usually a very good approximation. To preserve a close analogy to the rank 4 elasto-optical or photoelastic tensor p_{ijkl} relating strain and index change, we define the q -dependent index change as

$$\Delta B_{\mu\nu} = P_{\mu\nu ij} q_i q_j \quad (0.3)$$

where $\Delta B_{\mu\nu}$ is the change of the relative dielectric impermeability tensor B_{ij} from its $q=0$ value. (B_{ij} and related tensors are defined and discussed on page 243 of J. F. Nye, *Physical Properties of Crystals*. B_{ij} is the inverse of the dielectric tensor.) The tensor $P_{\mu\nu ij}$ we define here may or may not be defined the same way so a careful comparison is needed when working with actual values. In a cubic crystal system, a rank 4 tensor has only three unique nonzero components. Using a contracted notation (see J. F. Nye, *Physical Properties of Crystals*, near page 248), these components are

$$\begin{aligned} P_{1111} &\rightarrow P_{11} \\ P_{1122} &\rightarrow P_{12} \\ P_{1212} &\rightarrow P_{44} \end{aligned} \quad (0.4)$$

or P_{11} , P_{12} , and P_{44} . Note that the same three tensor components fully characterize the photoelastic response of a cubic material (a different tensor, of course, but with the same transformation properties). The dyad formed by $\bar{q}\bar{q}$ has to be modified to conform to the contracted index notation. The 3x3 tensor (dyad) representing $\bar{q}\bar{q}$ is replaced by a column vector with 6 components

$$\bar{Q} = \begin{bmatrix} q_1 q_1 \\ q_2 q_2 \\ q_3 q_3 \\ 2q_2 q_3 \\ 2q_1 q_3 \\ 2q_1 q_2 \end{bmatrix}. \quad (0.5)$$

[0041] The factors of 2 are needed to make the contracted index products reproduce the messier index summations of the original rank 4 tensor. Using these definitions, Eq.(0.3) can be rewritten

$$\begin{aligned}
B_{11}(\vec{q}) &= B_{11}(0) + P_{11}q_1^2 + P_{12}(q_2^2 + q_3^2) \\
B_{22}(\vec{q}) &= B_{22}(0) + P_{11}q_2^2 + P_{12}(q_1^2 + q_3^2) \\
B_{33}(\vec{q}) &= B_{33}(0) + P_{11}q_3^2 + P_{12}(q_1^2 + q_2^2) \\
B_{32}(\vec{q}) &= 2P_{44}q_2q_3 \\
B_{31}(\vec{q}) &= 2P_{44}q_1q_3 \\
B_{21}(\vec{q}) &= 2P_{44}q_1q_2
\end{aligned} \tag{0.6}$$

[0042] Given measured or theoretically calculated values for the three constants P_{11} , P_{12} , and P_{44} , Eq.(0.6) shows exactly how the dielectric impermeability tensor components are modified at short wavelength in a cubic system. Further analysis requires that we specify some given direction for the photon wavevector \vec{q} so that we know the components q_1 , q_2 , and q_3 . (Note that different definitions of the P tensor are possible. The definitions should be checked carefully before comparing results.) The dielectric impermeability tensor is used to define the index ellipsoid or optical indicatrix by the expression

$$B_{ij}x_i x_j = 1. \tag{0.7}$$

[0043] Thus, small changes in B_{ij} give rise to changes in index of refraction (including birefringence) and changes in the principal index axes (the eigenvectors of B). For a cubic crystal (in the $\vec{q} = 0$ limit), the impermeability tensor is diagonal and has three identical eigenvalues, which are $(1/n^2)$ for index of refraction n . Thus $B_{11}(0)$, $B_{22}(0)$, and $B_{33}(0)$ for our cubic system are each $(1/n^2)$.

[0044] We expect birefringence along [100] to vanish according to arguments given above, but as a check, we apply Eq.(0.6) for $\vec{q} = (q, 0, 0)$. Then the dielectric impermeability tensor components become

$$\begin{aligned}
B_{11}(\vec{q}) &= 1/n^2 + P_{11}q^2 \\
B_{22}(\vec{q}) &= 1/n^2 + P_{12}q^2 \\
B_{33}(\vec{q}) &= 1/n^2 + P_{12}q^2 \\
B_{32}(\vec{q}) &= 0 \\
B_{31}(\vec{q}) &= 0 \\
B_{21}(\vec{q}) &= 0
\end{aligned} \tag{0.8}$$

[0045] Note that the dielectric impermeability tensor for this case is still diagonal, but no longer has the same value for each element on the diagonal. However, since light is a transverse wave, only the B_{22} and B_{33} components are relevant for our case of light traveling in the $[100]$ direction. For this simple case there are two equal eigenvalues that correspond to any polarizations perpendicular to $[100]$. Intrinsic birefringence is the difference between these two equal values, i.e. zero. Even though the birefringence vanishes, the actual index of refraction is altered slightly by this term. The altered index of refraction is given by the expression

$$\Delta n = -\frac{1}{2} n^3 \Delta B = -\frac{1}{2} n^3 P_{12} q^2. \quad (0.9)$$

[0046] (See Nye again, page 252.) It will turn out that the index of refraction, whether birefringent or not, can be modified by terms of order 1 ppm for light propagation in different directions in the cubic crystal. Such intrinsic variation in the index of refraction should be accounted for in lens design modeling, in addition to the intrinsic birefringence.

The $\langle 111 \rangle$ case

[0047] As for $\langle 100 \rangle$, we have given a symmetry argument for the vanishing of the birefringence for light propagation down the $\langle 111 \rangle$ axis. Nevertheless, it is instructive to go through the algebra and demonstrate this. Consider a wavevector $\vec{q} = (q, q, q) / \sqrt{3}$. The normalization is chosen so that the magnitude is q and not $\sqrt{3}q$. The dielectric impermeability tensor components become

$$\begin{aligned} B_{11}(\vec{q}) &= 1/n^2 + q^2(P_{11} + 2P_{12})/3 \\ B_{22}(\vec{q}) &= 1/n^2 + q^2(P_{11} + 2P_{12})/3 \\ B_{33}(\vec{q}) &= 1/n^2 + q^2(P_{11} + 2P_{12})/3 \\ B_{32}(\vec{q}) &= 2P_{44}q^2/3 \\ B_{31}(\vec{q}) &= 2P_{44}q^2/3 \\ B_{21}(\vec{q}) &= 2P_{44}q^2/3 \end{aligned} \quad (0.10)$$

[0048] Now the dielectric impermeability tensor is not diagonal, so it is not as obvious what the indices of refraction are for different polarizations and the related birefringence. What is needed are the eigenvectors and eigenvalues of the dielectric

impermeability tensor, giving the principal axes and principal indices of refraction (after some manipulation). The dielectric impermeability tensor has the form of a 3x3 matrix

$$\begin{bmatrix} a & b & b \\ b & a & b \\ b & b & a \end{bmatrix}. \quad (0.11)$$

[0049] This matrix has one eigenvalue of $(a+2b)$, with eigenvector $(1,1,1)/\sqrt{3}$, and two degenerate eigenvalues of $(a-b)$, with eigenvectors of $(-1,1,0)/\sqrt{2}$ and $(-1,0,1)/\sqrt{2}$. (Because the two eigenvalues are the same, any linear combination of these eigenvectors is also an eigenvector.) The first principal axis is along the propagation direction, so is irrelevant. The second two are possible principal axes of polarization, but again they do not produce birefringence because the eigenvalues (and indices of refraction) are the same. As in the $\{100\}$ case, the actual index of refraction is slightly modified, this time to the value

$$\Delta n = -\frac{1}{2}n^3\Delta B = -\frac{1}{2}n^3(P_{11} + 2P_{12} - 2P_{44})q^2/3, \quad (0.12)$$

[0050] but the intrinsic birefringence is zero.

The $\langle 110 \rangle$ case

[0051] We have argued from symmetry that the intrinsic birefringence will not vanish for the $\langle 110 \rangle$ direction.

[0052] The algebraic proof that follows also gives a quantitative expression for the intrinsic birefringence. Consider a photon wavevector of $\vec{q} = (1,1,0)/\sqrt{2}$. The dielectric impermeability tensor becomes

$$\begin{aligned} B_{11}(\vec{q}) &= 1/n^2 + q^2(P_{11} + P_{12})/2 \\ B_{22}(\vec{q}) &= 1/n^2 + q^2(P_{11} + P_{12})/2 \\ B_{33}(\vec{q}) &= 1/n^2 + q^2P_{12} \\ B_{32}(\vec{q}) &= 0 \\ B_{31}(\vec{q}) &= 0 \\ B_{21}(\vec{q}) &= q^2P_{44} \end{aligned} \quad (0.13)$$

The dielectric impermeability tensor is a 3x3 matrix with the form

$$\begin{bmatrix} a & c & 0 \\ c & a & 0 \\ 0 & 0 & b \end{bmatrix} \quad (0.14)$$

with eigenvalues and eigenvectors

$$\begin{aligned} & (1/n^2 + q^2[(P_{11} + P_{12})/2 + P_{44}]), \quad (1,1,0)/\sqrt{2} \\ & (1/n^2 + q^2[(P_{11} + P_{12})/2 - P_{44}]), \quad (-1,1,0)/\sqrt{2} . \\ & (1/n^2 + q^2 P_{12}), \quad (0,0,1) \end{aligned} \quad (0.15)$$

[0053] Light is traveling the same direction as the first eigenvector, so the second and third represent the principal axes for the index of refraction. Now, finally, we find different values of index to order q^2 for polarization along $\{-1,1,0\}$ and $\{0,0,1\}$:

$$\begin{aligned} \Delta n_{-1,1,0} &= -\frac{1}{2} n^3 [(P_{11} + P_{12})/2 - P_{44}] q^2 \\ \Delta n_{0,0,1} &= -\frac{1}{2} n^3 P_{12} q^2 \end{aligned} \quad (0.16)$$

Birefringence for light traveling in the $\{110\}$ direction has its maximum value at

$$BR = \Delta n_{-1,1,0} - \Delta n_{0,0,1} = -\frac{1}{2} n^3 [(P_{11} - P_{12})/2 - P_{44}] q^2 \quad (0.17)$$

[0054] This is a very important equation. It gives the relation between tensor components and the largest intrinsic birefringence.

[0055] A glass, or any material that may be considered truly the same (on average) in every direction, has an even higher symmetry than a cubic crystal. In an isotropic material, a rank 4 tensor has only two independent components that may be taken as P_{11} and P_{12} . Isotropic materials obey the relation

$$P_{44} = (P_{11} - P_{12})/2. \quad (0.18)$$

[0056] Since every direction is equivalent, we may consider light propagation in a $\langle 110 \rangle$ direction and look for a nonzero birefringence. Then Eq. (0.17) applies, but with Eq.(0.18), we see that $BR=0$. This had to be so, because we could just have easily considered $\langle 100 \rangle$ or $\langle 111 \rangle$ directions, where $BR=0$. Since all directions

are equivalent, the intrinsic birefringence must vanish in every direction. This is an important advantage for glasses.

Index of refraction vs. direction

[0057] Given an index ellipsoid or impermeability tensor B_{ij} , it is possible to define the indices of refraction for different polarizations and directions of light propagation. This is the kind of information needed for doing lens design or aberration modeling. The problem is more complicated for intrinsic birefringence, however, because the tensor B_{ij} itself changes for different directions of propagation, as shown above. Equation (0.6) gives all the information, but needs to be manipulated for each choice of directions given by q_1 , q_2 , and q_3 . Some simplifications should be possible. For example, for directions associated with rotating a vector in any plane equivalent to the xy plane, the direction goes through the sequence $[100]$, $[110]$, $[010]$, $[\bar{1}10]$, $[\bar{1}00]$, $[\bar{1}\bar{1}0]$, $[0\bar{1}0]$, $[1\bar{1}0]$, and then back to $[100]$ again. As these rotations are considered, the birefringence goes from 0 to its peak value given by Eq.(0.17) and back to 0 with 4 cycles, following the expression

$$BR = \left(-\frac{1}{2} n^3 [(P_{11} - P_{12})/2 - P_{44}] q^2 \right) \sin(2\theta) \quad (0.19)$$

where θ is the angle from the x-axis. It gets more complicated when the ray direction does not lie in a plane parallel to a cube face.

[0058] To estimate the intrinsic contribution to birefringence at various wavelengths, we consider only the direction of largest birefringence and take a value of 6.5 nm/cm at 157 nm. The expression to consider is Eq.(1.17), or

$$BR_{peak} = \left(-\frac{1}{2} n^3 [(P_{11} - P_{12})/2 - P_{44}] q^2 \right). \quad (0.20)$$

[0059] A Sellmeier expression for index variation of CaF_2 gives $n(157 \text{ nm})=1.5586$. To fit $BR = 6.5 \text{ nm/cm}$, and with $q = 2\pi/\lambda$, we deduce $[(P_{11} - P_{12})/2 - P_{44}] = 0.000214 \text{ nm}^2$. We expect these tensor components to have a little dispersion vs. wavelength, presumably getting smaller at longer wavelengths. As a result, the predicted intrinsic birefringence will be a little larger

than should actually be observed. Thus, keeping the tensor elements fixed in value from 157 nm but considering dispersion in index and q, the following table may be constructed:

| lambda(nm) | q(1/nm) | n | BR(nm/cm) |
|------------|----------|----------|-----------|
| 147 | 0.042743 | 1.589 | 7.8 |
| 157 | 0.04002 | 1.5586 | 6.5 |
| 193 | 0.032555 | 1.5015 | 3.8 |
| 248 | 0.025335 | 1.468 | 2.2 |
| 253.65 | 0.024771 | 1.466 | 2.1 |
| 633 | 0.009926 | 1.432882 | 0.3 |

[0060] The intrinsic birefringence is 26 times larger at 147 nm than at 633 nm, of which 18 is due to $1/\lambda^2$ and the rest due to $q=0$ index variation. If these estimates are correct then intrinsic birefringence, viewed in a $\langle 110 \rangle$ direction, should be rather small at 633 nm but readily observable at 193 nm. Measured values gives 1.2 nm/cm at 253.65 nm, compared with estimate of 2.1, so the dispersion in the P constants makes the result by 633 nm even smaller.

[0061] To exhibit the complexity arising for directions off of $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$, consider a ray direction that stays in the xy plane but runs at some angle (e.g. between $\{100\}$ and $\{110\}$):

$$\bar{q} = (\cos(\theta), \sin(\theta), 0). \quad (0.21)$$

[0062] The eigenvectors for this case are not simply along \bar{q} and perpendicular to \bar{q} . It is important to point out that the ray direction in this case is not an eigenvector. In all the high symmetry cases considered previously, the ray direction was one of the eigenvectors (principal directions), but this is apparently not the case for a more general wavevector such as Eq.(0.21). In the special case in which we set $P_{44}=(P_{11}-P_{12})/2$, then the ray direction is always an eigenvector with eigenvalue $1/n^2+P_{11}q^2$ and the other eigenvectors are in the plane perpendicular to this, with degenerate eigenvalues $1/n^2+P_{12}q^2$. This merely reflects the consequences of being isotropic, as in a glass.

[0063] The eigenvalues for wavevector $\bar{q} = (\cos(\theta), \sin(\theta), 0)$ are given by

We claim:

1. A method of making a <194 nm calcium fluoride crystal optical lithography element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence, said method comprising:
 - providing an optical element optical calcium fluoride crystal with an input face {100} crystal plane,
 - forming said input face {100} crystal plane into an optical lithography element surface of an optical lithography element having an optical axis, said optical axis aligned with a <100> crystal direction of said optical calcium fluoride crystal.
2. A method as claimed in claim 1 wherein forming includes forming said optical calcium fluoride crystal into a lens element with a curved optical element surface, said lens element having a lens optical axis aligned with a <100> crystal direction of said calcium fluoride crystal and normal to said {100} calcium fluoride crystal plane.
3. A method as claimed in claim 1 wherein forming includes forming said optical calcium fluoride crystal into a beam splitter cube with a beam splitter cube face parallel to said {100} calcium fluoride crystal plane and a beam splitter optical axis aligned with a <100> crystal direction of said calcium fluoride crystal.
4. A <194 nm calcium fluoride crystal optical lithography element for transmitting wavelengths less than 194 nm with minimal birefringence, said optical lithography element comprised of an optical calcium fluoride crystal with a {100} crystal plane and a <100> crystal direction, said optical element having an optical axis aligned with said <100> calcium fluoride crystal direction.
5. A method of making a fluoride crystal optical element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence, said method comprising:
 - providing an optical element optical fluoride crystal with an input face {100} crystal plane,

forming said input face {100} crystal plane into an optical element surface of an optical element having an optical axis, said optical axis aligned with a <100> crystal direction of said optical fluoride crystal.

6. A method as claimed in claim 5 wherein forming includes forming said optical fluoride crystal into a lens element with a curved optical element surface, said lens element having a lens optical axis aligned with a <100> crystal direction of said crystal and normal to said {100} crystal plane.
7. A method as claimed in claim 5 wherein forming includes forming said optical fluoride crystal into a beam splitter cube with a beam splitter cube face parallel to said {100} crystal plane and a beam splitter optical axis aligned with a <100> crystal direction of said crystal.
8. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of calcium.
9. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of barium.
10. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of strontium.
11. An optical element for transmitting wavelengths less than about 194 nm with minimal birefringence, said optical element comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction, said optical element having an optical axis aligned with said <100> crystal direction.
12. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of calcium .

13. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of barium .
14. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of strontium .
15. An optical element as claimed in claim 11 wherein said optical element is a lens element with a curved optical element surface and a lens optical axis aligned with said $\langle 100 \rangle$ crystal direction.
16. An optical element as claimed in claim 11 wherein said optical element is a beam splitter cube with a beam splitter cube face parallel to said $\{100\}$ crystal plane and a beam splitter optical axis aligned with said $\langle 100 \rangle$ crystal direction.
17. A below 194 nm wavelength transmitting lens, said lens comprised of a cubic optical fluoride crystal with a $\{100\}$ crystal plane and a $\langle 100 \rangle$ crystal direction, said lens having a curved optical surface and an optical axis, said optical axis aligned with said $\langle 100 \rangle$ crystal direction and normal to said $\{100\}$ crystal plane.
18. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of calcium.
19. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of barium.
20. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of strontium.
21. A below 194 nm wavelength transmitting beam splitter cube, said beam splitter cube comprised of a cubic optical fluoride crystal with a $\{100\}$ crystal plane and a $\langle 100 \rangle$ crystal direction, said beam splitter cube having a beam splitter cube

face parallel to said {100} crystal plane and an optical axis aligned with said <100> crystal direction.

22. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of calcium.

23. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of barium.

24. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of strontium.

AMENDED CLAIMS

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We claim:

1. A method of making a <194 nm calcium fluoride crystal optical lithography element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence, said method comprising:
 - providing an optical element optical calcium fluoride crystal with an input face {100} crystal plane,
 - forming said input face {100} crystal plane into an optical lithography element surface of an optical lithography element having an optical axis, said optical axis aligned with a <100> crystal direction of said optical calcium fluoride crystal,
 - wherein said formed optical lithography element having an optical axis aligned with a <100> crystal direction is used in an optical lithography system for transmitting wavelengths <194nm.
2. A method as claimed in claim 1 wherein forming includes forming said optical calcium fluoride crystal into a lens element with a curved optical element surface, said lens element having a lens optical axis aligned with a <100> crystal direction of said calcium fluoride crystal and normal to said {100} calcium fluoride crystal plane.
3. A method as claimed in claim 1 wherein forming includes forming said optical calcium fluoride crystal into a beam splitter cube with a beam splitter cube face parallel to said {100} calcium fluoride crystal plane and a beam splitter optical axis aligned with a <100> crystal direction of said calcium fluoride crystal.
4. A <194 nm calcium fluoride crystal optical lithography element for transmitting wavelengths less than 194 nm with minimal birefringence, said optical lithography element comprised of an optical calcium fluoride crystal with a {100} crystal plane and a <100> crystal direction, said optical element having an optical axis aligned with said <100> calcium fluoride crystal direction.

5. A method of making a fluoride crystal optical element for transmitting wavelengths less than about 194 nm along an optical axis with minimal birefringence, said method comprising:
- providing an optical element optical fluoride crystal with an input face {100} crystal plane,
 - forming said input face {100} crystal plane into an optical element surface of an optical element having an optical axis, said optical axis aligned with a $\langle 100 \rangle$ crystal direction of said optical fluoride crystal,
 - wherein said fluoride crystal element transmits wavelengths $<194\text{nm}$ along an optical axis aligned with a $\langle 100 \rangle$ crystal direction of said optical fluoride crystal.
6. A method as claimed in claim 5 wherein forming includes forming said optical fluoride crystal into a lens element with a curved optical element surface, said lens element having a lens optical axis aligned with a $\langle 100 \rangle$ crystal direction of said crystal and normal to said {100} crystal plane.
7. A method as claimed in claim 5 wherein forming includes forming said optical fluoride crystal into a beam splitter cube with a beam splitter cube face parallel to said {100} crystal plane and a beam splitter optical axis aligned with a $\langle 100 \rangle$ crystal direction of said crystal.
8. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of calcium.
9. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of barium.
10. A method as claimed in claim 5 wherein said optical fluoride crystal is comprised of strontium.

11. An optical element for transmitting wavelengths less than about 194 nm with minimal birefringence, said optical element comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction, said optical element having an optical axis aligned with said <100> crystal direction,
wherein said optical element having an optical axis aligned with said <100> crystal direction transmits <194nm wavelengths.
12. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of calcium.
13. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of barium.
14. An optical element as claimed in claim 11 wherein said optical fluoride crystal is comprised of strontium.
15. An optical element as claimed in claim 11 wherein said optical element is a lens element with a curved optical element surface and a lens optical axis aligned with said <100> crystal direction.
16. An optical element as claimed in claim 11 wherein said optical element is a beam splitter cube with a beam splitter cube face parallel to said {100} crystal plane and a beam splitter optical axis aligned with said <100> crystal direction.
17. A below 194 nm wavelength transmitting lens, said lens comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction, said lens having a curved optical surface and an optical axis, said optical axis aligned with said <100> crystal direction and normal to said {100} crystal plane,
wherein said lens having an optical axis aligned with said <100> crystal direction and normal to said {100} crystal plane transmits <194nm wavelengths.

18. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of calcium.
19. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of barium.
20. A below 194 nm wavelength transmitting lens in accordance with claim 17, said cubic optical fluoride crystal comprised of strontium.
21. A below 194 nm wavelength transmitting beam splitter cube, said beam splitter cube comprised of a cubic optical fluoride crystal with a {100} crystal plane and a <100> crystal direction, said beam splitter cube having a beam splitter cube face parallel to said {100} crystal plane and an optical axis aligned with said <100> crystal direction.
22. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of calcium.
23. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of barium.
24. A below 194 nm wavelength transmitting beam splitter cube in accordance with claim 21, said cubic optical fluoride crystal comprised of strontium.

FIG. 1

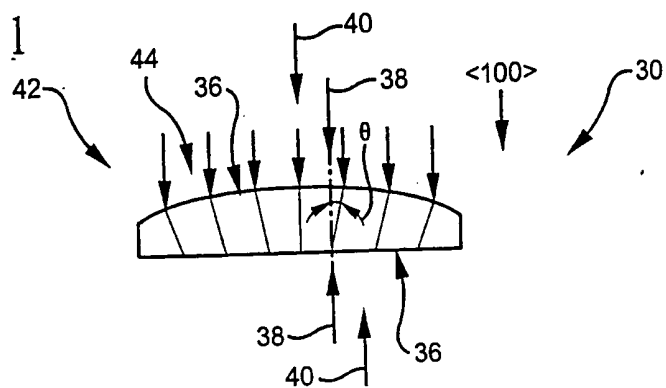


FIG. 1a

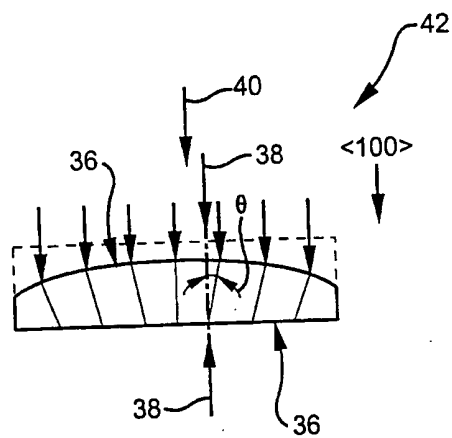
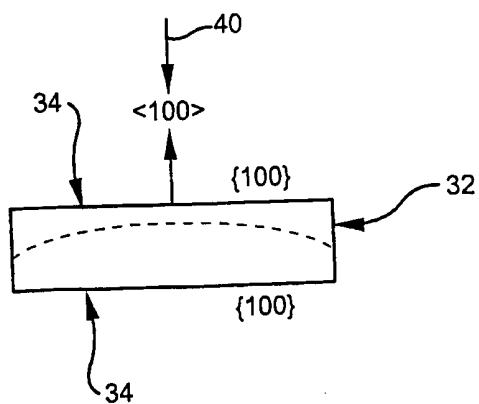


FIG. 1b



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FIG. 2

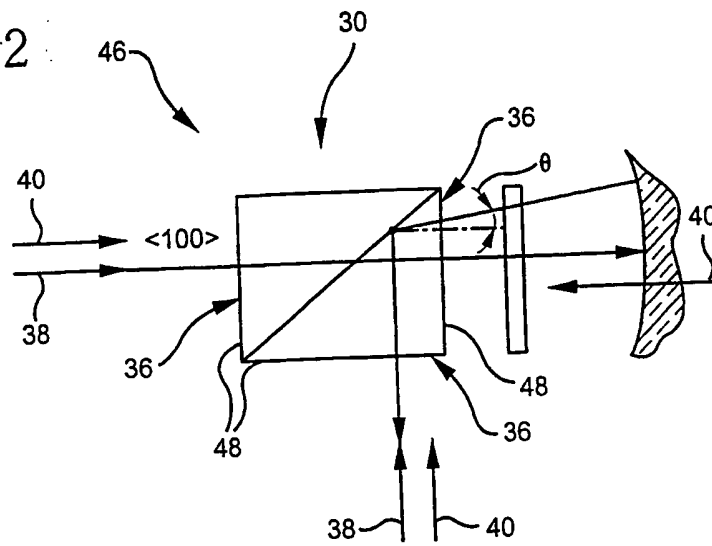
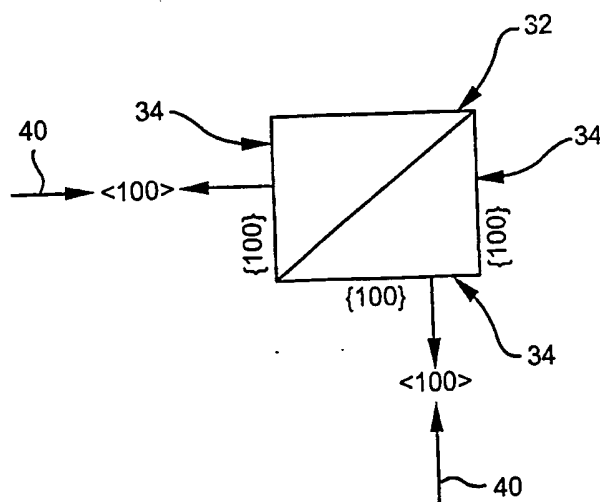


FIG. 2a



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FIG. 3

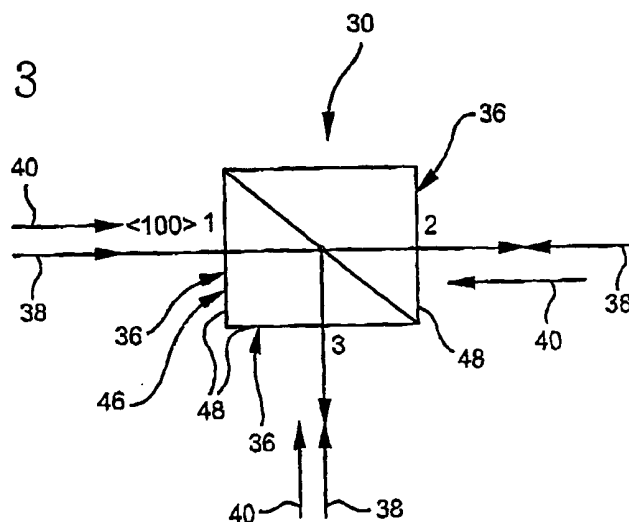
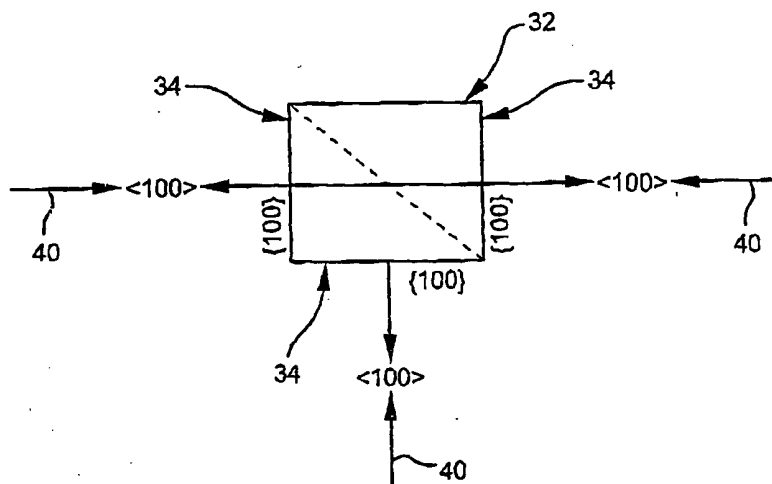


FIG. 3a



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/15100

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : G02B 5/30,13/14, 27/10,27/14,27/12; F21V 9/06; G02F 1/01

US CL : 359/321,322,323,350,352,355,361,618,129,634,640

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 359/321,322,323,350,352,355,361,618,129,634,640

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | US 2001/0008540 A1 (OBA et al) 19 JULY 2000; page1, sections 9,10,14,19-21, 34 &36; page 4, section 77&85;see figure 6. | 1-24 |
| X | US 6,201,634 B1 (SAKUMA et al) 13 MARCH 2001, column 1, lines 20-25, column 2,lines 10-19&65-67, col. 5, lines 40-50. | 1-24 |

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search

31 March 2003 (31.03.2003)

Date of mailing of the international search report

02 MAY 2003

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

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Authorized officer

Georgia Epps

Telephone No. 703 308 0956

INTERNATIONAL SEARCH REPORT

PCT/US02/15100

Continuation of B. FIELDS SEARCHED Item 3:

East

Search terms: lithography, inteferometer, calcuim, flouride, crystal

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